The Chloride Induced Localised Corrosion of Aluminium and Beryllium:
A Study by Electron and X-ray Spectroscopies

Christopher F. Mallinson
MChem

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The Surface Analysis Laboratory
Department of Mechanical Engineering Sciences
University of Surrey
Guildford, Surrey, GU2 7XH

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Abstract

Beryllium is an important metal in the nuclear industry for which there are no suitable replacements. It undergoes localised corrosion at the site of heterogeneities in the metal surface. Corrosion pits are associated with a range of second phase particles. To investigate the role of these particles in corrosion, a safe experimental protocol was established using an aluminium alloy as a corrosion material analogue. The 7075-T6 alloy had not previously been investigated using the experimental methodology used in this thesis. This work led to the development of the experimental methodology and safe working practices for handling beryllium.

The range and composition of the second phase particles present in S-65 beryllium billet were identified using a combination of SEM, AES, EDX and WDX. Following the identification of a range of particles with various compositions, including the AlFeBe₄ precipitate which has been previously associated with corrosion, the location of the particles were marked to enable their repeated study.

Attention was focused on the microchemistry in the vicinity of second phase particles, as a function of immersion time in pH 7, 0.1 M NaCl solution. The corrosion process associated with different particles was followed by repeatedly relocating the particles to perform analysis by means of SEM, AES and EDX.

The use of traditional chlorinated vapour degreasing solvents on beryllium was investigated and compared to two modern commercially available cleaning solutions designed as drop-in replacements. This work expanded the range of solvents suitable for cleaning beryllium and validated the conclusions from previous thermodynamic modelling.

Additionally, a new experimental methodology has been developed which enables the acquisition of chemical state information from the surface of micron scale features. This was applied to sub-micron copper and iron particles, as well as a copper intermetallic.
Acknowledgements

I would like to thank Prof. John Watts his constant drive and enthusiasm for research has pushed me and enabled me to achieve more than I thought possible and for keeping me going until the end. And for putting up with endless knocks on his door.

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Many thanks to Dr. Mark Baker for his useful discussions. I would also like to thank Dr. Rossana Grilli for training me to use the Microlab and helping me solve many of the early instrument crashes.

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Thanks to my teachers who motivated to me study science ever further and in particular to Marcus Rutland who helped ingrain my passion for chemistry and pushed me to begin my university education and to Jeremy Hinks who let me into Southampton University for my undergraduate degree.

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Lastly, I would like to thank my Dad and Mum for their unwavering support and encouragement and my girlfriend Ishna, who puts up with my gibberish about electrons and x-rays while making me want to work harder and be better every day.

I am forever indebted to John and Ann for not giving up on me after an exceedingly difficult and trying first 12 months, without their support I would not have been able to continue my doctorate.

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## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AA</td>
<td>Aluminium alloy</td>
</tr>
<tr>
<td>AES</td>
<td>Auger electron spectroscopy</td>
</tr>
<tr>
<td>ARXPS</td>
<td>Angle resolved x-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>BE</td>
<td>Binding energy</td>
</tr>
<tr>
<td>CAE</td>
<td>Constant analyser energy</td>
</tr>
<tr>
<td>CMA</td>
<td>Cylindrical mirror analyser</td>
</tr>
<tr>
<td>CRR</td>
<td>Constant retard ratio</td>
</tr>
<tr>
<td>DDI</td>
<td>Deionised distilled water</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive x-ray spectroscopy</td>
</tr>
<tr>
<td>Epit</td>
<td>Pitting potential</td>
</tr>
<tr>
<td>Erp</td>
<td>Repassivation potential</td>
</tr>
<tr>
<td>FAT</td>
<td>Fixed analyser transmission</td>
</tr>
<tr>
<td>FEG</td>
<td>Field emission electron gun</td>
</tr>
<tr>
<td>FIB</td>
<td>Focussed ion beam</td>
</tr>
<tr>
<td>FOV</td>
<td>Field of view</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width half maximum</td>
</tr>
<tr>
<td>HCP</td>
<td>Hexagonal close packed</td>
</tr>
<tr>
<td>HSA</td>
<td>Hemispherical sector analyser</td>
</tr>
<tr>
<td>IMFP</td>
<td>Inelastic mean free path</td>
</tr>
<tr>
<td>KE</td>
<td>Kinetic energy</td>
</tr>
<tr>
<td>LANL</td>
<td>Los Alamos national laboratory</td>
</tr>
<tr>
<td>LLNL</td>
<td>Lawrence Livermore national laboratory</td>
</tr>
<tr>
<td>MMSE</td>
<td>Mercury/mercurous sulphate electrode</td>
</tr>
<tr>
<td>OCP</td>
<td>Open circuit potential</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>RLM</td>
<td>Reflected light microscope/microscopy</td>
</tr>
<tr>
<td>SAM</td>
<td>Scanning Auger microscope/microscopy</td>
</tr>
<tr>
<td>SCC</td>
<td>Stress corrosions cracking</td>
</tr>
<tr>
<td>SCE</td>
<td>Saturated calomel electrode</td>
</tr>
<tr>
<td>SDD</td>
<td>Silicon drift detector</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope/microscopy</td>
</tr>
<tr>
<td>SKPM</td>
<td>Scanning Kevin probe microscopy</td>
</tr>
<tr>
<td>SiLi</td>
<td>Silicon lithium (detector)</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra high vacuum</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet light</td>
</tr>
<tr>
<td>WDX</td>
<td>Wavelength dispersive x-ray spectroscopy</td>
</tr>
<tr>
<td>XAES</td>
<td>X-ray excited Auger electron spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>ZAF</td>
<td>Atomic mass-absorbance-fluorescence</td>
</tr>
<tr>
<td>SiGe</td>
<td>Silicon germanium alloy</td>
</tr>
<tr>
<td>SGOI</td>
<td>Silicon germanium on insulator</td>
</tr>
</tbody>
</table>
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Chapter 1 - Introduction

1.1 Introduction

The problem that was investigated throughout this thesis was the chloride induced localised corrosion of beryllium. The experimental objectives were designed to enable the study of beryllium, which is a highly toxic material, in a safe and controlled manner. Beryllium is a light metal that undergoes localised corrosion. Corrosion is believed to initiate at the site of second phase particles which interrupt the homogeneity of the surface oxide layer. A number of different phases have been implicated in the formation of corrosion pits including: AlFeBe₄, FeBe₅, TiBe₁₂, BeO, Be₂C and elemental silicon. Of these, AlFeBe₄ has received the most attention as it is one of the most numerous intermetallics that can form in beryllium. It is present in beryllium as a deliberate precipitate to remove free aluminium and improve high temperature ductility. Therefore, it cannot be removed from structural grades of the metal without adversely affecting the material properties.

The majority of the current understanding about the corrosion of beryllium is based upon electrochemical measurements of samples tested using cyclic voltammetry. This has provided a generalised view of the corrosion behaviour of the metal. These investigations have shown that the pitting potential is affected to a greater extent by the chloride ion concentration in solution than the solution pH. With logarithmic and linear relationships observed respectively. It has also been shown that crystallographic orientation plays a role in the general corrosion of beryllium. The basal plane of the hexagonal close packed unit cell, beryllium adopts, is the most resilient to corrosion resulting in needle like crystals in pit interiors.

The recent focus applied to beryllium has been the examination of the appearance of the surface before and after polarisation in corrosive solutions, in an attempt to understand the role of the second phase particles in the corrosion of beryllium. From this recent work it is understood that pitting initiates at second phase particles when anodic polarisation, in the pitting regime, is applied. Performing the polarisation acts to reinforce any galvanic differences between particles and the matrix and defects in the oxide layer. Whilst it is useful to understand the electrochemical corrosion processes which occur as a result of these driven conditions, they represent a model system to test the corrosion in an accelerated aging trial. Therefore, the behaviour that was observed in this work may not accurately represent the behaviour of second phase particles at the open circuit potential at which a beryllium specimen would be under typical applications.

A more detailed understanding of the exact microchemistry, as a function of time, involved in the localised corrosion, associated with the different second phase particles is required. This must also be under corrosive conditions which are more relevant to industrial beryllium applications. This understanding will contribute towards the establishment of a model with the aim of predicting the rate of corrosion of commercial beryllium materials.

Aluminium is a light metal which undergoes pitting corrosion in similar chloride concentrations as beryllium. It also has a range of second phase particles of a similar size to those observed in S-65 beryllium.
The corrosion of an aluminium alloy was studied as an analogue. This acted as an initial learning tool in the use of the spectrometers and microscopes required for the project, allowed for the validation of the experimental method and functioned as a test of the initially outlined safety precautions for beryllium.

The experimental investigation performed in this thesis was designed to meet the requirements of the sponsor. These requirements were achieved by identifying a range of second phase particles with different compositions and monitoring their behaviour in a corrosive solution over time. During the project there was a need to reliably relocate the same regions of the surface and ensure they remained in a near constant geometry for the study of the individual second phase particles. This was needed as the sample had to be removed from the spectrometer to perform the corrosion steps. A number of particle compositions needed to be examined to encompass the range of different phases present in beryllium and their corrosion behaviour.

Finished metal components are usually vapour degreased using chlorinated solvents to remove various soils introduced to the metal surface during machining operations. The compatibility between these solvents and beryllium has not been widely studied, with only three solvents previously addressed experimentally and a further seventeen investigated thermodynamically. The thermodynamic investigation suggested requirements for the formation of metal salt corrosion precursors. As such, there is a need further examine the solvents theoretically investigated to test the predictions of the modelling. The use of traditional, standalone, chlorinated solvents is being phased out and replaced with commercial cleaning solutions designed as drop in replacements. However, these have as yet not been tested for compatibility with beryllium and require experimental investigation.

In an attempt to obtain further information about the passive film of intermetallics and the surface chemistry involved with the corrosion processes associated with second phase particles, a new experimental technique was developed. The new technique has been named “proximal XPS” because the x-rays required for generating photoelectrons are generated locally and not at a remote anode. The method was developed using micrometer sized particles deposited on an aluminium substrate and eventually extended to sub-micron copper and iron particles.

1.2 Aims

The aim of the work presented in this thesis was to gain a better understanding of the microchemistry involved at the surface of beryllium as a result of the corrosion process induced by a chloride containing solution. Techniques including: Auger electron spectroscopy (AES), energy dispersive x-ray spectroscopy (EDX), wavelength dispersive x-ray spectroscopy (WDX), x-ray photoelectron spectroscopy and scanning electron microscopy (SEM) were used to characterise the samples. Attention was focused on examining the morphological and compositional changes of second phase particles, present at the metal surface, after exposure to a 0.1 M NaCl solution.
1.3 Objectives

The primary objective required from the outset of this project was to establish a safe working protocol for the analysis of beryllium. No investigative techniques that could lead to damage of beryllium or the generation of particulates could be undertaken before this objective was met.

Prior to undertaking any corrosion investigation of beryllium, the initial acquisition of reference quality spectra was required. Little, modern good-quality spectra for beryllium and beryllium compounds existed prior to the work produced in this thesis. As such, these were collected to enable the identification of specific spectral components for beryllium chemical states. Additionally, prior to corrosion a thorough investigation of the second phase particles present in beryllium was required in order to understand their size, distribution and composition.

In support of the previous objective, an experimental trial using a non-toxic material, prior to the analysis of beryllium, was required to enable risk-free learning about the techniques and the physical processes involved. Once comfortable with the analysis procedures and safety protocols, beryllium could be analysed within the University laboratory in a safe and controlled manner so as not to pose a risk to personnel working in the laboratory.

An additional objective was to develop an understanding and practical expertise in the instruments and the relevant theory that would be needed in this project. This included understanding the individual strengths and limitations of the various techniques employed in this work.

1.4 Structure of the thesis

1.4.1 Thesis

Following this brief introduction, the thesis chapters are organised as follows:

- In Chapter 2 an overview of the existing literature available on the corrosion of beryllium is presented. The primary themes from the literature include: the effects of pH and chloride concentration and the effect of crystallographic orientation on the corrosion process. Additionally, a major focus is placed on the range of second phase particles believed to be involved in the initiation of pitting corrosion. Finally a brief summary of the existing literature utilising the same investigative techniques, as used in this thesis, for the study of pitting corrosion in other materials is reviewed.

- In Chapter 3 the surface and bulk analysis techniques used in this project are described together with the pertinent experimental theory. The main focus is on the use of AES, EDX and SEM, as these were available on the Thermo Scientific MICROLAB 350 microscope.

- In Chapter 4 a short literature review of the corrosion of AA7075-T6 is provided, followed by a description of the multi-technique characterisation of the aluminium alloy during a corrosion
investigation. The investigation focused on three intermetallics of different composition. These were characterised with the same set of AES, EDX and SEM analyses after consecutive exposure times of 15, 45 min, 2, 4, 8 and 16 hours in 3.5 wt.% KCl, pH 7 solution.

- In Chapter 5 the electron and x-ray analysis of beryllium and beryllium compounds are presented and discussed. Some of the particular challenges associated with the analysis of beryllium are also highlighted and discussed.

- In Chapter 6 the multi-technique characterisation of S-65 beryllium during a corrosion investigation is described. The investigation focused on a number of intermetallics of different size and composition. These were marked and characterised with AES, EDX and SEM analyses after consecutive exposure times of 15, 45 min, 2, 4, 8, 16, 32, 64 and 128 hours in a 0.1 M NaCl, pH 7, solution.

- In Chapter 7 the effect of exposing beryllium to chlorinated solvent vapours, as analysed by XPS, is described. A comparison between commercial cleaning solutions and traditional, readily available, chlorinated solvents is also made. (The vapour degreasing and XPS analysis performed using the ESCALAB Mk II, shown in this chapter was performed by a MEng student, S. Kozlowski, with intensive experimental support from myself).

- In Chapter 8 presents the preliminary results and initial optimisation of a new investigative, surface analysis, technique. The technique enables the acquisition of chemical state information from the surface of sub-micron particles and surface features.

- In Chapter 9 the overall results of this work are discussed and models for the observed corrosion phenomena are proposed.

- In Chapter 10 the conclusions of the work carried out in this thesis are summarised and a clear roadmap of possible future work is provided.

1.4.2 Annex of publications

1.4.2.1 Publications list

This annex contains the 14 publications on which I was an author or a co-author. In addition to these, copies of the posters presented at conferences during this project are included. Below is a list of the work contained within:

1. XPS of Beryllium and Beryllium Oxide, C. F. Mallinson and J. E. Castle, Surface Science Spectra, 2013, 20, 1, 86


5. XPS Analysis of Small Particles by Proximal X-ray Generation, J. E. Castle, R. Grilli, **C. F. Mallinson**, *Surface and Interface Analysis*, 2014, 46, (10-11), 949


10. XPS Examination of the Oxide Layer Formed on Kovar following Pre-oxidation, **C. F. Mallinson**, S. Tardio, P. M. Yates, M. T. Staff, J.A. Fernie, J. F. Watts. *Surface Science Spectra*, 2015, 22, 1, 58


Three additional manuscripts are currently in preparation to be submitted in 2015, these are shown below with their working titles and the journal titles they are planned to be submitted to:


1.4.2.2 Poster presentations
1. UKSAF 2013 Summer, Newcastle, July 2013.
2. ECASIA, Sardinia, Italy, October 2013.
5. AVS, Baltimore, USA, November 2014.
7. NAMSEC AWE, Aldermaston, January 2015
9. ECASIA, Granada, Spain, September 2015.

1.4.2.3 Oral presentations
3. ECASIA, Granada, Spain, September 2015.
Chapter 2 - Literature Review

2.1 Introduction
The focus of this chapter is to review the available literature on beryllium corrosion, examine the extent of knowledge that has already been achieved in the field and investigate how this project will contribute to further the understanding of beryllium corrosion. While there has been research into the corrosion of beryllium at high temperatures for use as cladding materials in future fusion reactors and significant research into the protection of beryllium components from corrosion with protective coatings, these are outside the scope of this project and this review.

Despite the widespread use of beryllium in aerospace and nuclear applications, limited literature is available on beryllium corrosion compared to other light metals. Work on beryllium is limited because of the specific specialist applications in which the metal is used and more importantly the high risk posed to the health and safety of personnel working with beryllium.

Beryllium is highly toxic by inhalation. Particles <10 μm are able to penetrate deep into the lungs and can lead to a chronic lung disease known as berylliosis. The link between beryllium and lung disease has been studied since the early 1940s [1]. Much of the beryllium research dates back to before the 1960s when there was the largest interest in beryllium for various nuclear applications. Much of this early literature is based upon internal reports from national laboratories based in the United States and the beryllium producer, Materion Brush, formerly Brush Wellman.

2.2 Extraction of beryllium from ore
Beryllium is present within the crust of the earth at concentrations of 4-6 ppm and over 50 beryllium containing minerals have so far been identified [2]. Two of these minerals are considered commercially viable for beryllium extraction these are: Beryl (3BeO.Al₂O₃.6SiO₂) and Bertrandite (4BeO.2SiO₂.H₂O).

Whereas Bertrandite is soluble in acid, the silicate structure of Beryl renders is insoluble and so a different extraction process is required. For Beryl, the Kjellgren sulphate process is used [3]. In this process the ore is heated to 1650-1900 °C where it is then quenched, destroying the silicate structure. The Beryl is then heated to 900-1000 °C and sulphuric acid is added. The resulting slurry contains beryllium sulphate and impurities consisting of mainly aluminium, silica and iron. Further processes including filtration and the use of chelating agents are carried out to remove the various metal impurities, before sodium is added to precipitate crude beryllium hydroxide. The costly and time intensive process required to extract beryllium from Beryl, led to the development of alternative extraction processes, such as the route for Bertrandite.

Bertrandite is initially leached using boiling sulphuric acid to produce a solution of beryllium sulphate containing a range of sulphated impurities including: iron, sodium and aluminium. The leach solution is
mixed with an organic extraction solution of an alkyl acid phosphate, typically di-2-ethylhexyl-phosphoric acid, in a water immiscible solvent such as kerosene [3].

The waste aqueous solution from this step contains no detectable levels of beryllium and contains the majority of the sodium impurities. Most of the remaining metal ions are contained within the organic phase. The addition of aqueous ammonium carbonate to the organic phase leads to the formation of aqueous beryllium ammonium carbonate and precipitates of iron and aluminium. The waste organic phase contains few metal ions. Filtration of the aqueous phase leads to almost complete removal of iron and aluminium with only a slight loss of beryllium. Heating this solution to 70 °C for 45 minutes precipitates material rich in the remaining iron and aluminium, which is removed by filtration. Heating the filtered solution further to 94 °C leads to precipitation of mixed beryllium compounds. When this precipitate is filtered and processed by heating to 165 °C in deionised water, high purity beryllium hydroxide is obtained.

The beryllium hydroxide from both the Beryl and Bertrandite processing routes can be mixed at this stage and dissolved in ammonium bifluoride, forming ammonium fluoroberyllate [(NH$_4$)$_2$BeF$_4$]. This is then crystallised and thermally decomposed at 1000 °C to beryllium fluoride and NH$_4$F gas. The beryllium fluoride is reduced, using magnesium at 900 °C in graphite crucibles, to produce beryllium metal and magnesium fluoride. The molten beryllium is then cast into billets [3].

2.3 Production of beryllium metal

Beryllium can be produced by casting and powder routes. While casting of beryllium can be successful using standard techniques, the smallest achievable grain size is ~100-200 μm [3,4]. Since the strength, ductility and machineability of beryllium are all adversely affected by a large grain size, casting is not utilised for mainstream metal production.

Production via powder metallurgy is achieved by the mechanical processing of vacuum cast ingots. These are reduced to chips on lathes and are then attrition milled. The milling action works the beryllium chips against stationary and rotating beryllium plates. The gradual reduction in particle size is primarily a result of basal plane [0001] cleavage. As such the powder produced from attrition milling has a tendency for platelet shape morphology.

Two other techniques for powder production are also utilised: impact grinding and ball milling. Impact grinding is slowly replacing attrition milling because of the desire to limit the anisotropic nature of the metal produced. Impact grinding involves the blasting of beryllium chip against a beryllium target. The resultant powder is more equiaxed than the metal produced by attrition as cleavage occurs along a number of crystallographic planes, although when a finer powder is desired, ball milling is used.

The beryllium powder is consolidated by vacuum hot pressing at 1025-1125 °C and ~8 MPa. The resulting beryllium billets achieve > 99% of the theoretical density and have a typical grain size of 10-20 μm.
production of bulk metal via powder metallurgy leads to a large increase in the beryllium oxide content, as shown by the compositions of beryllium in Table 2.1.

Table 2.1 Examples of impurities present in three different types of beryllium: S-200D was produced from a powder route, the ingot was produced from casting and the single crystal produced from molecular beam deposition

<table>
<thead>
<tr>
<th>Beryllium grade</th>
<th>Be (at.%)</th>
<th>BeO (at.%)</th>
<th>Al (ppm)</th>
<th>C (ppm)</th>
<th>Fe (ppm)</th>
<th>Mg (ppm)</th>
<th>Si (ppm)</th>
<th>Other (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-200D</td>
<td>98.0</td>
<td>2.0</td>
<td>3000</td>
<td>2800</td>
<td>3400</td>
<td>1500</td>
<td>1500</td>
<td>750</td>
</tr>
<tr>
<td>Ingot</td>
<td>99.3</td>
<td>0.05</td>
<td>725</td>
<td>700</td>
<td>1400</td>
<td>-</td>
<td>400</td>
<td>200</td>
</tr>
<tr>
<td>Single crystal</td>
<td>99.99</td>
<td>&lt;0.01</td>
<td>18</td>
<td>-</td>
<td>&lt;4</td>
<td>-</td>
<td>&lt;130</td>
<td>270</td>
</tr>
</tbody>
</table>

The increase in beryllium oxide concentration is a consequence of the formation of a thin oxide layer on the beryllium powder particles during processing. However, this is useful because the oxide particles pin grain boundaries and prevent large grain growth.

2.4 Beryllium crystal structure

Beryllium adopts a hexagonal close-packed (HCP) crystal structure. Lattice parameters $a$ and $c$ are required to characterise the HCP unit cell. For beryllium the lattice parameters are: $a = 0.2285$ nm and $c = 0.3583$ nm. In an ideal HCP unit cell the ratio of lattice parameters $c/a = 1.633$. At this value, the packing of atoms within the cell are such that the atoms in the upper and lower basal planes almost touch those atoms in the middle of the unit cell. Various crystallographic planes within the HCP unit cell of beryllium are highlighted in Figure 2.1.

Most metals will deviate from the ideal $c/a$ ratio. If the ratio is greater than the ideal, the spacing between the atoms along the $c$ axis is increased and if the ratio is smaller than the atoms along the $c$ axis are compressed. The $c/a$ ratio for beryllium is particularly low at 1.57 and beryllium has the smallest unit cell of all the HCP metals. The unusually large shift from the ideal ratio causes distortion in the crystal lattice this is a result of the covalent bonding character of bulk beryllium metal.

![Figure 2.1 A schematic of the HCP beryllium unit cell, together with a number of important crystallographic planes.](image)

2.5 Corrosion of beryllium

2.5.1 Background

A pH-potential or Pourbaix diagram for beryllium is shown in Figure 2.2. The diagram shows the theoretical conditions of corrosion, immunity and passivation for beryllium at 25 °C in pure water, free of aggressive...
ions and under equilibrium conditions. The diagram gives an indication of the processes that will occur under a given set of conditions. The lines (a) and (b) represent the reduction of water to hydrogen and the oxidation of water to oxygen respectively.

![Pourbaix diagram for beryllium at standard conditions](image)

The diagram describes how beryllium shows a wide passive region in the pH range 4 to 10. In this region the surface is covered with a protective layer of Be(OH)$_2$. If the pH is decreased and the solution becomes more acidic, the beryllium corrodes via the dissolution of beryllium in the form Be$^{2+}$. If the pH increases and the solution become more alkaline, corrosion of the beryllium occurs in the form of Be$_2$O$_2^2$ and BeO$_2^2$ [5]. The impressive passivity of beryllium in solutions of pure deionised water over the pH range 2-12.5 is shown in Figure 2.3. Beryllium is passive over the entire potential range tested and does not pit in the absence of aggressive ions. However, these conditions are rarely encountered in the real world, as aggressive ions such as: F, Cl and SO$_4$ are ubiquitous.

![Beryllium polarisation curve as a function of pH in pure water](image)

**2.5.2 Deposition corrosion**

It has been indicated that trace levels of copper present in corrosive media can considerably increase the corrosion rate of beryllium. Copper is present in beryllium at an incredibly low concentration of <400 ppm, as such it is believed that the copper in solution either originated from impure water or as contamination from the surrounding environment [7]. Copper is able to adversely affect the corrosion resistance of
beryllium by depositing onto the cathodic areas of the metal surface. Copper, being a particularly noble metal could increase the potential of the cathodic regions and accelerate the removal of the surrounding anodic material. This form of corrosion has been observed for aluminium alloys. Copper at concentrations of >0.02-0.05 ppm in a solution to which aluminium is exposed is considered to be the threshold for pitting. Other noble metals which have been observed to result in deposition corrosion include: lead, mercury, nickel and tin [8,9].

2.6 Precautions to take when handling beryllium components

2.6.1 Minimise the risk of corrosion

The presence of aggressive chloride ions has long been known to result in accelerated corrosion of beryllium [10]. Some simple guidelines were produced by Materion Brush in order to minimise corrosion problems on unprotected beryllium surfaces [11]:

- Minimise contact with tap water
- Maintain surface cleanliness - avoid hand contact/fingerprinting
- Take care in machining operations to minimise surface damage - lapping will not cover up prior bad practice

Tap water contains traces of chloride and sulphate ions. When a beryllium sample is rinsed in tap water the surface contaminants become concentrated in the evaporating water droplets during drying. This leaves the metal vulnerable during storage to any condensation that may form and provides a site for corrosion. The risk to finished metal pieces can be minimised by thoroughly rinsing samples with deionised water prior to drying.

Touching finished or semi-finished parts should be avoided without the use of gloves as fingerprints provide a source of contamination from salts which are able to etch the sample surface. Machined metal surfaces are normally etched to remove microcracks produced from machining. Precision components that cannot be etched are typically lapped. This leaves behind a significant number of microcracks which are susceptible to crevice corrosion.

Other sources of chlorine contamination include chlorinated solvents which are used to degrease components and plastic piping in cleaning systems. Contact with plastics including polystyrene folders or sheets can result in localised etching and subsequent corrosion. A polyethylene bag can be used as an effective barrier between beryllium and chloride containing materials. Storage of components should be in dry, non-condensing environment that is free of chloride contamination. A number of recommendations for storage have been made [12]:

- Ensure the metal surface is chloride free prior to storage
- Maintain a dry environment
- Do not allow materials of unknown compatibility to touch one another
2.6.2 The storage environment for beryllium

During long term storage beryllium can be exposed to environments which are particularly unfavourable for the prevention of corrosion. The metal can be stored at temperatures reaching ~50 °C [5]. In addition there is a possibility of moisture forming on the metal, as the storage environment is not humidity controlled. The surface of the beryllium is also frequently contaminated with traces of chlorine from vapour degreasing procedures. Contamination can also be introduced from the packaging material surrounding the metal.

2.7 Electrochemical potential difference

2.7.1 Introduction

The electrochemical potential difference between a metal and the environment is the basic driving force for corrosion. A conductive path between the two sites must exist for electrons to flow and for corrosion to continue. The potential relative to a standard is different for each metal. When two different metals are placed in a conductive electrolyte or are held in intimate contact with one another such that a conductive pathway is formed between them, the potential difference between the metals results in electrons flowing from the more active metal to the more noble metal. The result is that the more active metal corrodes faster than it would do compared to the uncoupled metal.

As a consequence of the heterogeneities present in many metals, different potentials can occur within a metal itself. This can be considered as galvanic corrosion on a microscopic scale. Some sites become anodic and others cathodic. If a second phase particle acts as an anode to the metal matrix it will dissolve preferentially to the matrix and eventually leave a hole or a pit. If the particle acts as a cathode the surrounding metal matrix will dissolve and the second phase particle can be undermined and dislodged from the matrix, again resulting in a hole or pit.

At the anodic, sites a metal such as beryllium is oxidised and will dissolve as per Equation 2.1:

\[ \text{Be} (s) \rightarrow \text{Be}^{2+} (aq) + 2e^- \quad (2.1) \]

The corresponding reaction to balance the equation could be the production of hydroxyl ions at the cathodic sites, as per Equation 2.2:

\[ 2 \text{H}_2\text{O} (l) + 4e^- + \text{O}_2 (g) \rightarrow \text{H}_2(g) + 4\text{OH}^- (aq) \quad (2.2) \]

Each reaction is known as a half cell reaction as it forms one half of a complete reaction. The electrode potential is recorded as the potential difference between the metal and a reference electrode. The hydrogen half cell \((\text{H}_2/\text{H}^+)\) is used as zero potential. The half cells are recorded at standard conditions which are: 1 M aqueous solution of both the metal and hydrogen ions at 25 °C. Table 2.2 shows half cell reactions for a range of metals including beryllium referenced to the hydrogen half cell equation.
Table 2.2 Half cell reactions under standard conditions for a range of metals, referenced to the hydrogen half cell potential

<table>
<thead>
<tr>
<th>Metal-ion equilibrium</th>
<th>Electrode potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au⁺/Au</td>
<td>1.69</td>
</tr>
<tr>
<td>Pt⁺/Pt</td>
<td>1.20</td>
</tr>
<tr>
<td>Ag⁺/Ag</td>
<td>0.80</td>
</tr>
<tr>
<td>Cu²⁺/Cu</td>
<td>0.34</td>
</tr>
<tr>
<td>H⁺/H₂</td>
<td>0.00</td>
</tr>
<tr>
<td>Fe³⁺/Fe</td>
<td>-0.04</td>
</tr>
<tr>
<td>Ni²⁺/Ni</td>
<td>-0.25</td>
</tr>
<tr>
<td>Fe²⁺/Fe</td>
<td>-0.45</td>
</tr>
<tr>
<td>Zn²⁺/Zn</td>
<td>-0.76</td>
</tr>
<tr>
<td>Al³⁺/Al</td>
<td>-1.66</td>
</tr>
<tr>
<td>Be²⁺/Be</td>
<td>-1.85</td>
</tr>
<tr>
<td>Mg²⁺/Mg</td>
<td>-2.36</td>
</tr>
</tbody>
</table>

The measured electrode potential is dependent upon the type of electrolyte, the concentration and the temperature of the solution when the measurements are made. This gives rise to a number of potential or galvanic series. For example, the galvanic series for sea water is taken as the cell potentials measured in a solution of 3.5 wt.% NaCl at 25 °C. This solution approximates to sea water that can be used in place of real seawater in a laboratory environment.

The order of metals within Table 2.2 is based upon their tendency to dissolve in solution. At the top are the most noble and at the bottom are the most active metals. The more negative the electrode potential, the further to the left the equilibrium lays and the metal is a strong reducing agent. The more positive the electrode potential, the further to the right the equilibrium lays and the stronger the oxidising agent the metal ion is. Beryllium is found near the bottom of the galvanic series as it has a highly negative potential. However, this is under standard conditions of the metal which does not take into account the highly adherent and insulating protective oxide film. The metal oxide can have a dramatic effect on the electrode potential. It is expected that second phase particles rich in elements that are cathodic compared to beryllium will be cathodic in the metal. There have been some studies to investigate galvanic behaviour of various second phase particles and these will be discussed in a later section.

An important consideration when investigating galvanic effects is the difference in surface area between the cathode and anode. The flux of current between the anode and cathode is independent of their respective sizes. However, the current density does change with area. From Faraday's Law, the rate of corrosion depends upon the current density at the anode. If a system is setup allowing current to flow from the cathode to the anode the anode will corrode. If the same current flows but the size of the anode is reduced by a factor of ten then the current density at the anode will increase by a factor of ten also and the anode will corrode ten times faster. Therefore, in order to minimise the rate of galvanic corrosion it is desirable for the anode to be large and the cathode to be small.

In the design of systems where dissimilar metals are placed in intimate contact or have contact through conductive solution, the galvanic effect can be managed by coating or plating the metal surfaces. By ensuring that the potential difference between the metals does not exceed certain values for certain
environments, the degree of corrosion can be minimised. General “rules of thumb” for harsh environments, with high humidity and salt content a difference of < 0.15 V is desired. For normal environments at room temperature, that are humidity controlled, a difference of < 0.25 V is desired. For the best environments, where temperature and humidity are controlled, even a difference as high as 0.50 V might not result in corrosion [13].

A significant proportion of the literature available on beryllium corrosion relies upon electrochemical measurements because of this a short section is included here to describe a cyclic polarisation graph and some of the general terms used in this Chapter. Schematic graphs of cyclic polarisation curves showing forward and reverse scans are shown in Figure 2.4 (a + b). In the forward scan (a) the open circuit potential (OCP) or the corrosion potential (E\text{corr}) is the voltage of the metal that is being tested against a reference electrode under steady state (equilibrium conditions), when no potential or current is applied to the metal. If a metal with a more positive OCP is electrically connected to a metal with a more negative OCP the metal with the lower OCP will preferentially corrode.

![Cyclic Polarisation Graph](image)

**Figure 2.4 (a) A schematic of a cyclic polarisation graph showing a forward anodic scan and (b) schematic showing the reverse cathodic scan.**

The current density at which the OCP is measured is known as the corrosion current (I\text{corr}). As the potential is increased further beyond the OCP the current density increases until a stable region is reached. This stable region represents the oxide film on the metal. Eventually when the applied anodic potential reaches a critical value a break down occurs and the current density rapidly increases. This critical value is known as the pitting potential (E\text{pit}) and represents the point at which the passive film breaks down and corrosion begins. The potential range between the OCP and E\text{pit} is known as the passive range, the size of which gives an indication of the strength or protectiveness of the oxide layer.

In the reverse scan (b) the potential at which the cathodic sweep intersects with the first sweep is known as the repassivation potential (E\text{rp}) and the current at which this occurs is known as the passivation current (I\text{pass}). If a potential is applied above Erp then pitting corrosion can initiate, if a potential is applied below E\text{rp} then no new pitting events occur but formed pits can continue to corrode.
2.7.2 Galvanic couples with beryllium

Accelerated corrosion of beryllium has been reported for beryllium coupled to 1100, 6061, 6053, 7072 and 4353 aluminium alloys, as well as 347 stainless steel [10]. Results were obtained prior to the establishment of the modern aluminium alloy nomenclature and so the old alloy designations have been replaced with the modern equivalent [14]. Galvanic attack has also been observed for beryllium in contact with brass and mild steel, in the presence of cutting oils and machining coolant.

For 1100 aluminium alloy: contact with beryllium under static conditions in pure water, at 85 °C, pH 6.0 with equal surface areas, the beryllium was preferentially attacked. The general corrosion rates were ~32 μm year\(^{-1}\) for beryllium and ~4 μm year\(^{-1}\) for aluminium. Under dynamic conditions, with a solution flow rate of 2 m s\(^{-1}\), corrosion was accelerated on both metals, although beryllium was still preferentially attacked. The corrosion rates were ~48 μm year\(^{-1}\) for beryllium and ~20 μm year\(^{-1}\) for aluminium. It was noted that the pitting frequency increased fivefold moving from static to dynamic tests. Similar results were obtained for all of the tested beryllium-aluminium alloy couples [10].

In the case of beryllium coupled to type 347 stainless steel, under the same experimental conditions as for the aluminium samples, beryllium showed accelerated corrosion, with a general rate of 60 μm year\(^{-1}\). The stainless steel showed negligible attack. The corrosion rates for beryllium coupled to aluminium or steel were three to five times greater than those obtained for uncoupled control specimens, indicating that beryllium was acting anodically [10].

Galvanic effects have also been observed in beryllium welds. The most commonly used filler metal for beryllium welds is Al-12 wt.% Si. While the resulting welds allow the joining of beryllium components, there is a possibility of galvanic effects from the weld. Copper sulphate has been used to identify this possibility by plating copper onto the cathodic regions. 100 ppm of copper sulphate was added to a solution of 0.01 M NaCl and a beryllium weld was immersed for 5 minutes. Following the immersion the aluminium-silicon weld was plated with copper while the surrounding beryllium was unaffected by the copper ions [6].

Polarisation studies have also been performed on both the host beryllium and the aluminium-silicon phase formed during welding. Solutions were at ambient aeration in 0.1 M NaCl at pH 7. Figure 2.5 shows polarisation curves collected from the investigation, they illustrate that the open circuit potential (OCP) for the aluminium-silicon phase is considerably more positive than beryllium. This indicates that under the conditions studied, when the two are coupled, the beryllium will be anodically attacked with the Al-Si weld acting as the cathode [15].
2.8 Effect of chlorine ion concentration on corrosion

The earliest corrosion data available for beryllium is regarded as being erratic and having a general lack of reproducibility [16]. Test results appeared to vary which was a consequence of the poor metal quality used early in the development of beryllium metal [10]. Some of the earliest corrosion studies based upon second phase particles present in beryllium were carried out in the late 1940s and early 1950s. One investigation was performed by adding varying amounts of iron, aluminium, silicon and beryllium carbide to melts of vacuum cast and hot-pressed beryllium in order to study their effect on the corrosion resistance of beryllium. Iron concentrations of 0.23, 0.34 and 0.40 wt.% were studied as well as 0.2 wt.% silicon in vacuum cast samples. Aluminium concentrations of 0.30, 0.44, 0.73 and 1.05 wt.% and beryllium carbide concentrations of 0.11, 0.23 and 0.26 wt.% were also incorporated into hot pressed beryllium.

The beryllium samples were left for 13 months in distilled water at 85 °C and the pH was maintained between 5.5 and 6.5. The rate of corrosion for all of the beryllium samples was determined to be between 1.8 to 2.5 μm year⁻¹. Pitting was observed on all of the samples within three months and slight variations in corrosion rates for the different samples could not be attributed to the presence of any one impurity. However, it was noted that the frequency of pits on the aluminium containing specimens, ~8 pits cm⁻², was more than double that of the controls and other impurity added specimens ~3 pits cm⁻² [10]. A similar investigation had been performed a few years previously where the tests were performed at 300 °C, the results indicated that when the total impurity content was low, the corrosion resistance of beryllium was good [10].

An early study compared the behaviour of extruded beryllium in oxygen free and oxygen saturated water at 90 °C, which contained either 1 or 30,000 ppm of chloride. The oxygen concentration appeared to have little effect on the corrosion resistance of beryllium in water containing 1 ppm of chloride. However, in the oxygen saturated water that contained 30,000 ppm of chloride, corrosive attack was severe. A weight loss of up to 9.5 mg cm⁻² was obtained under these conditions compared to only 0.1 mg cm⁻² on the samples exposed to the low chloride concentration solutions [10]. Samples of extruded beryllium exposed to chloride
concentrations of 1, 5 and 10 ppm in aerated distilled water at 90 °C were studied over a period of 30 days. As the chloride concentration was increased so too was the degree of corrosive attack. The results from the study are shown in Figure 2.6. A solution containing 1 ppm of chloride had a corrosion rate of ~117 μm year⁻¹. Solutions containing greater concentrations of chloride caused more severe pitting [10].

![Figure 2.6 Graph of the weight lost from beryllium samples kept in three different concentrations of chloride containing water held at 90 °C over a 30 day period.](image)

Exposure of beryllium to HCl has been observed to result in rapid general corrosion of the surface. Short exposures led to etching of the surface, while long exposures led to the formation of black needle like crystals which turned the solution black [17]. This effect has not been observed for beryllium exposed to HF, H₂SO₄ or HNO₃ but has been observed for beryllium exposed to HClO₄ and HBr at higher concentrations. Further investigation showed severe uniform etching across the entire beryllium surface and darkening of the solution when exposed to 0.1 M or 1 M KCl [18].

Effects have been observed that suggest that halide ion size has a strong influence on the corrosion of beryllium. I⁻, Br⁻ and Cl⁻ ions are all able to diffuse to the surface of the metal with equal ease but the smaller Cl⁻ ion can penetrate the surface oxide film to form a damaging metal salt [18]. The ease with which these salts can form is related to their size. Other anions such as SO₄²⁻, NO₃⁻, PO₄³⁻ and F⁻, either as a result of their size or hydration sphere, cannot easily penetrate the film and so corrosion can only occur at weak points in the oxide film.

Numerous electrochemical studies have been performed to investigate the effect of chloride ion concentration and pH on the corrosion of beryllium. The first of these studies focused on the corrosion of beryllium welds and polycrystalline S-200D beryllium in aqueous solutions of NaCl with concentrations of 0.0001, 0.001, 0.01 and 0.1 M [15]. Figure 2.7 shows the polarisation curves collected during this investigation. The solutions were deaerated with argon, kept at 25 °C and had a pH of 7.0.
The pitting potential was found to increase with increasing chloride concentration. With a logarithmic relationship, as shown in Equation 2.3:

\[
Pitting \ potential \ (V) = -0.064 \times \log[Cl^-] - 0.999 \quad (2.3)\]

Where:

The pitting potential \(E_{\text{pit}}\) is in volts vs. the Saturated Calomel Electrode (SCE) and \([Cl^-]\) is the chloride concentration in mol L\(^{-1}\) [15].

This work was later repeated and expanded to include a 1 M KCl solution studied at 25 °C at pH 7.0. The results obtained from this investigation are shown in Figure 2.8 and the relationship has been confirmed in three separate investigations [15,19,20]. Following the further work, the relationship was refined and is shown in Equation 2.4:

\[
Pitting \ potential \ (V) = -0.067 \times \log[Cl^-] - 1.01 \quad (2.4)\]

Similar logarithmic relationships for the chloride concentration to the pitting potential have been found for aluminium and for 18/8 stainless steel, showing relationships of -0.091 V/ log[Cl\(^-\)] and -0.088 V/log[Cl\(^-\)] respectively [21,22]. These relationships show that aluminium and stainless steel are more sensitive to changes in chloride concentration than beryllium.
Following an extensive investigation into the effect of second phase particles on the corrosion behaviour of three different grades of beryllium using cyclic polarisation, similar logarithmic relationships were found between the pitting potential and the chloride ion concentration. With both the age and materials processing route of beryllium known to affect the corrosion properties, three forms of beryllium, S-65 bar, S-65 billet and P-10 bar were selected for testing. Each sample was tested in solutions of 0.0001 M, 0.001 M and 0.01 M KCl at pH 7 and at room temperature. The S-65 bar was additionally tested in 0.1 M KCl. Relationships between the chloride concentration and pitting potential vs. the SCE are shown in Table 2.3 [23]. The relationships are similar to those found previously [15,19].

Table 2.3 Relationship between pitting potential and chloride concentration for three grades of beryllium

<table>
<thead>
<tr>
<th>Sample</th>
<th>Relationship $\text{E}_\text{pit}$(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-65 bar</td>
<td>$-0.033 \log[\text{Cl}] - 1.052$</td>
</tr>
<tr>
<td>S-65 billet</td>
<td>$-0.036 \log[\text{Cl}] - 1.084$</td>
</tr>
<tr>
<td>P-10 bar</td>
<td>$-0.030 \log[\text{Cl}] - 1.044$</td>
</tr>
</tbody>
</table>

### 2.9 Effect of ions other than chlorine

#### 2.9.1 Corrosive effect of sulphate ions

In addition to the effect of chloride ions, the effect of sulphate ions (sodium sulphate source) on the pitting corrosion beryllium has also been studied. The solutions used in the study contained concentrations of 5, 10 and 15 ppm of sulphate ions. Pitting was present on all of the beryllium samples tested with corrosion rates measured as 8-12 μm year$^{-1}$. This rate was almost five times faster than control samples exposed to only deionised water [10]. The rate of corrosion was greatly increased when the sulphate ion source was sulphuric acid instead of sodium sulphate, rates of 25, 50 and 152 μm year$^{-1}$ were reported. This was a consequence of the decrease in the pH of the solution.

Exposure of beryllium to $\text{H}_2\text{SO}_4$ was believed to result in the formation of the soluble $\text{BeSO}_4$ salt and hydrogen. When beryllium was exposed to 0.33 M $\text{K}_2\text{SO}_4$ only light localised attack was observed and a large fraction of the surface remained shiny and uncorroded. When the specimen was repolished, it was found that the sub-surface region was severely penetrated and honeycombed [18].
2.9.2 Corrosive effect of fluoride ions

Beryllium is known to be attacked by HF, resulting in the formation of the soluble BeF₂ salt and hydrogen. A polished vacuum cast 99% beryllium specimen exposed to concentrated HF at room temperature was observed to remain smooth even after long exposure times, although SEM analysis showed some fine structure at grain boundaries [17]. Similar results were also reported for beryllium S-200D, following exposure to 0.01 M or 0.1 M KF + K₂SO₄ the surface appeared to suffer only light localised attack, with a large fraction of the surface remaining shiny. However, when the specimen was repolished it was found, as for the K₂SO₄ exposed sample, that the sub-surface region was severely penetrated and honeycombed with the removal of 20-30% of the material [18].

In an effort to further the understanding of beryllium corrosion in aqueous solutions, polarisation curves for beryllium S-200D were produced for solutions of 0.0001 M, 0.001 M, 0.01 M and 0.1 M NaF at pH 7 at 25 °C [15]. Figure 2.9 shows the results from this investigation. It was found that for the lowest concentrations of fluoride, the pitting potential was similar to the equivalent chloride concentration at -0.742 V and -0.773 V vs. SCE respectively. Pitting was observed on samples exposed to the 0.0001 M and 0.001 M NaF solutions. No region of passivity was observed for the sample exposed to the 0.001 M solution. After exposure to the two more concentrated fluoride solutions 0.01 M and 0.1 M, uniform corrosion was observed and the sample underwent attack at OCP. It is believed that a complex salt film is formed on the surface of the beryllium when exposed to these concentrations [15].

![Figure 2.9 Polarisation curves for beryllium as a function of fluoride concentration [15].](image)

2.9.3 The corrosive effect of metal ions

The effect of copper and iron ions in solution on the corrosion rate has also been studied. Both metals were found to accelerate corrosion [10]. For copper, added as copper sulphate, corrosion rates were reported as 15 - 40 μm year⁻¹. For iron, added as iron sulphate, corrosion rates were reported as 5 - 57 μm year⁻¹. These were reported as being much greater than sulphate control samples in solutions containing 1 - 10 ppm of iron and 0.1 - 0.5 ppm of copper.
2.9.4 Effect of multiple ions

Discussed in section 2.14 is the packaging material Celotex. It is possible to extract a solution containing relatively high concentrations of chloride and sulphate ions, as well as trace concentrations of bromide and fluoride ions from the material. While the effect of chloride and sulphate ions combined in solution has not investigated for beryllium, a study has been produced on the synergistic effect of chloride and sulphate ions on pitting corrosion of copper. In this investigation the pit generation rate $\lambda_o$ was used as a measure for the aggressiveness of the corrosive ion. This is taken as the time taken for the first pitting events to occur when the surface is examined using electrochemical polarisation. The rate was found to have a complex relationship with the concentrations of the ions. Figure 2.10 shows the generalised effect when chloride ions were injected simultaneously into a solution with a known concentration of sulphate ions (0.01, 0.02 and 0.05 M). $\lambda_o$ showed three response regions: In region 1) at low Cl$^-\,$ concentration ($10^{-6}$-$10^{-4}\,M$), increasing the Cl$^-\,$ content increased $\lambda_o$. In region 2) at medium Cl$^-\,$ concentration ($10^{-4}$-$10^{-2}\,M$), increasing the Cl$^-\,$ content decreased $\lambda_o$ and in region 3) at high Cl$^-\,$ concentration (>10$^{-2}\,M$), increasing the Cl$^-\,$ content rapidly increased $\lambda_o$ [24].

![Figure 2.10](image)

Figure 2.10 Schematic showing the general effect of changing chloride ion concentration from $1 \times 10^{-7}$ to 1 M on the pitting germination rate of a copper surface [24].

As part of the investigation into Celotex packaging material, a sample of S-200F beryllium was exposed to a solution of Celotex extract. Figure 2.11 shows the polarisation curve collected from a sample of beryllium exposed to the deaerated Celotex solution. The concentration of Cl$^-\,$ was 0.008 M and the F$^-\,$ concentration was 0.007 M. The solution had a pH of 4 and was kept at room temperature.
The pitting potential, in the Celotex solution, was found to be -0.850 V vs. SCE, this was in good agreement with the value calculated for a solution containing [Cl\textsuperscript{-}] of 0.008 M which was -0.865 V. No region of passivity was observed for the beryllium and large increases in current density were observed for slight changes in potential. Examination of the beryllium surface following the investigation showed heavy pitting.

The final part of an investigation into the passivity and breakdown of beryllium in aqueous environments involved the comparison between the polarisation curves produced from solutions of 0.1 M NaCl, 0.1 M NaF and a mixture of 0.1 M NaCl with 0.1 M NaF. This enabled observations to be made which could build upon previous work, whereby multiple aggressive anions were found in the corrosive Celotex solution. The polarisation curves from the investigation are shown in Figure 2.12.

The addition of small concentrations of fluorine, less than 0.01 M NaF, to the 0.01 M NaCl solution resulted in an increase in the passive current density but did not affect the chloride pitting potential. Pitting occurred in all three of the solutions. No region of passivity was observed for the fluoride containing solutions. Solutions with a higher concentration of fluoride > 0.01 M NaF only displayed localised attack in the presence of the chloride.
2.10 The effect of pH on corrosion

The pH of an environment is known to have a strong influence on the corrosion behaviour of a material in the absence of aggressive ions. The investigation into the electrochemical behaviour of beryllium in pure water that was shown in Figure 2.3 was expanded to include solutions with pH 1 and pH 2 at higher anodic currents. The expanded electrochemical polarisation curves are shown in Figure 2.13. These show a significant increase in current density at the open circuit potential (OCP) at pH 1. A small region of passivity was observed at pH 2, which was much smaller than that observed for higher pH solutions. General corrosion was also observed at the OCP for the pH 1 solution. The electrochemical studies were in good agreement with long-term real world observations that beryllium remained shiny in service for years in the absence of corrosive media [25].

![Figure 2.13 Polarisation curves of the current density as a function of pH in the absence of aggressive ions [19](image)](image)

As part of a previously mentioned study into the effect of chloride ion concentration on the corrosion of polycrystalline beryllium and beryllium welds, the effect of pH was also briefly investigated [15]. Figure 2.14 shows the polarisation curves for a sample of S-200F beryllium exposed to deaerated solutions of 0.1 M NaCl at pH 1, 2, 7 and 12. Inspection of the curves shows that beryllium actively corrodes at the open circuit potential in 0.1 M NaCl solutions with a pH <2 and exhibits a large passive range at pH 12.5. Pitting was observed on the metal exposed to the pH 7 and pH 12.5 solutions. It was noticed in this investigation that the surfaces of the samples exposed to low pH did not show pitting and appeared black, this was in agreement with other investigations [17,18].
Samples of S-200D beryllium were tested using cyclic polarisation in solutions containing no chloride at pH of 2.0, 4.6, 7.0, 10.7 and 12.5 and the passive current density was recorded for each [15]. The data was combined with the data collected from another study investigating pH [19]. The results from both investigations are shown in Figure 2.15. The passive current density and the corrosion current density followed a similar relationship and showed a minimum in the pH range 4.5 to 10.7. The large passive range is in agreement with that represented by the Pourbaix in Figure 2.2.

The overall effect of pH on the pitting potential is shown in Figure 2.16. A potential change of only 40 mV was observed across the pH range 2-12.5, compared to the 250 mV change observed for solutions with chloride ion concentrations 0.0001 M to 1 M. The solutions were 0.1 M NaCl, adjusted in pH using diluted NaOH or HCl, deaerated and kept at room temperature [19]. The linear relationship between solution pH and pitting potential is shown in Equation 2.5:

\[
Pitting\ potential\ (V) = 0.0003\ pH - 0.96 \quad (2.5)
\]
In addition to the previous studies a further electrochemical investigation into the corrosion of polycrystalline beryllium, as a function of pH, was carried out for 0.1 M NaCl solutions over the pH range 3 to 9. The exact grade of beryllium was not reported. Figure 2.17 shows the graph produced from the results of this investigation. The relationship between pitting potential and pH was found to be a linear relationship similar to that found for S-200F beryllium [26]. As is shown in Equation 2.6:

\[ \text{Pitting potential (V)} = 0.014 \text{pH} - 1.028 \]  (2.6)

The results of the investigations into the effect of chloride ion concentration and pH showed that the corrosion of beryllium is more dependent upon the chloride concentration than the pH as the pitting potential-pH relationship is linear while the pitting potential-chloride concentration relationship is logarithmic.
2.11 Crystallographic orientation effects

Beryllium is highly anisotropic and this is reflected in the physical and mechanical properties of finished metal components. Improvements in metal processing have minimised the anisotropy of hot pressed beryllium. However, some anisotropy is still present in most beryllium components. Different rates of corrosion are expected for certain crystal orientations simply as a consequence of the density of atoms within a plane. It is expected that for a hexagonal close packed crystal structure, corrosion would preferentially occur along the prism planes, as basal plane cleavage requires breaking six bonds compared to the four needed for either prism plane. Table 2.4 highlights the difference in atomic surface density of the two prism planes and the basal plane. The basal plane has the highest atomic surface density of the three planes. The crystallography of pure beryllium is characterised by a hexagonal unit cell with the features shown in Table 2.5.

Table 2.4 Information regarding the three lattice planes encountered in corrosion literature. The plane positions in the unit cell, surface area and atomic density are listed

<table>
<thead>
<tr>
<th>Plane</th>
<th>Diagram</th>
<th>Surface area (m²)</th>
<th>Atoms in plane</th>
<th>Atomic surface density (atoms m⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0001) Basel</td>
<td></td>
<td>0.136x10⁻¹⁸</td>
<td>3</td>
<td>2.2x10¹⁹</td>
</tr>
<tr>
<td>(0110) Type I Prism</td>
<td></td>
<td>0.082x10⁻¹⁸</td>
<td>1</td>
<td>1.2x10¹⁹</td>
</tr>
<tr>
<td>(1120) Type II Prism</td>
<td></td>
<td>0.141x10⁻¹⁸</td>
<td>2</td>
<td>1.4x10¹⁹</td>
</tr>
</tbody>
</table>

Table 2.5 Crystallography of beryllium

<table>
<thead>
<tr>
<th>Space group</th>
<th>Lattice parameters (nm)</th>
<th>Angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P6₃/mmc</td>
<td>a 0.2286 b 0.2286 c 0.3584</td>
<td>α 90 β 90 γ 120</td>
</tr>
</tbody>
</table>

In a number of metal systems the nature of pitting corrosion is related to the crystallographic orientation of the surface grains in a polycrystalline material. Working a material causes an alignment of the grain structure which can radically change the corrosion behaviour compared to the unworked form. As a consequence of manufacturing processes involving rolling or extrusion, beryllium will tend to align with the basal plane parallel to the surface of the produced metal [16]. Therefore, it is important to consider that as manufacturing techniques have improved over time, the degree of anisotropy has decreased and so differences in the corrosion behaviour are expected for different ages of beryllium.

Observations showing evidence for crystallographic effects on the corrosion of beryllium were first reported in 1962 [17]. Crystal needles were imaged on the sample surface after exposure of vacuum cast beryllium to concentrated HCl. Further investigations into the effect have been performed by several authors [26–29]. Further investigations studied the corrosion characteristics of high purity beryllium single crystals. The samples were polished to orientations close to the basal (0001), type I prism (1010) and type II prism (1120) planes. Each of the samples was tested using cyclic polarisation in pH 7, 0.01 M NaCl solution at room
temperature. The beryllium single crystals used in this study were alloyed with ~0.3 at.% copper in solid solution, this was not thought by the authors to have had a significant effect upon the results [26]. The cyclic polarisation curves from this study are shown in Figure 2.18.

![Cyclic polarisation curves](image)

**Figure 2.18** Cyclic polarisation curves from three beryllium single crystals: (0001), (1120) and (1010) in 0.0.1 M NaCl at pH 7 [26].

The investigation showed that the passivation current ($I_{pass}$) was almost identical for the type I (1010) and type II (11̅20) prism planes but was noticeably less for the basal plane (0001), at 43.4 µA and 10.7 µA respectively. The passive range for each of the three planes was different. The 1010 prism and 1120 planes were 0.462 V and 0.363 V respectively while the basal plane was significantly lower at 0.102 V. The size of the passive range, corrosion potential – pitting potential ($E_{corr} - E_{pit}$), was found to be inversely proportional to the atomic surface density as shown in Table 2.4. It was found that for all three single crystals the repassivation potential ($E_{rp}$) was identical at -0.864 V.

Similar results from cyclic polarisation studies were also obtained from a study carried out on the (0001), (1010) and (11̅20) crystal surfaces in deaerated 0.01 M NaCl [28]. The results from these are shown in Figure 2.19. The pitting potential ($E_{pit}$) was found to decrease with crystal orientation in the order (0001) > (1010) > (11̅20). Unlike the previous study it was found that $E_{rp}$ also followed the same crystallographic effect as $E_{pit}$ [28]. The region representing the potential difference between $E_{pit}$ and the OCP was large for (0001) and (1010) single crystals being > 100 mV and smaller for the (11̅20) single crystal. The higher the pitting potential of a surface, the smaller the population density of pits, likewise the reverse is true. The expression $E_{pit} - E_{rp}$ represents the extent of pit growth. This implies that a surface orientation with a large $E_{pit}$ and with a large ($E_{pit} - E_{rp}$) would experience fewer, but deeper, pits [28].
It was concluded that a dominant factor in the corrosion of beryllium was the orientation of particular grains and suggested that grain boundaries and second phase particles were not a major factor in corrosion. While this argument may hold true for beryllium single crystals with impurity concentrations of < 20 ppm, applying this conclusion to real polycrystalline beryllium components with typical impurity concentrations more than 250x greater at > 5000 ppm, should be cautioned [26].

The most recent experimental investigations with polycrystalline commercial grades of beryllium have shown that the dominant factor in corrosion is the second phase particles. Electron backscattered diffraction (EBSD) maps of polycrystalline beryllium have shown no correlation between pit initiation sites and the crystallographic orientation of specific grains [30].

### 2.12 Morphology of corrosion pits

Corrosion pit morphology of polycrystalline beryllium after electrochemical polarisation in 0.01 M KCl solution has been observed to be of the same size and shape as the grain morphology. The corrosion pits were not hemispherical and parallel plates of unattacked beryllium were observed in the pit interior [31]. Figure 2.20 shows the pit morphologies of the basal plane (0001) and the prism planes (1010) and (11\(\overline{2}0\)), following cyclic polarisation in 0.01 M NaCl at pH 7. The pits in the basal (0001) plane showed jagged and poorly defined pit perimeters. The two prism plane crystals showed pits with crystallographically orientated fibres all aligned in the same direction. Pits in polycrystalline beryllium appeared as a mix of the two morphologies as shown in Figure 2.21. The jagged edges of the basal plane grains are observed together with aligned lamella in different orientations.
Figure 2.20 SEM micrographs of different beryllium single crystal orientations following cyclic polarisation. (a and b) are the basal plane (0001), (c and d) are the type one prism plane (1010) and (e and f) are the type two prism plane (11\(\overline{2}0\)) [26].

Further investigation on the same single crystal samples reported that on the (1010) and (11\(\overline{2}0\)) surfaces, the pit interiors were characterised by crystallographically oriented parallel plates of unattacked beryllium, an example of which is shown in Figure 2.22 [28]. It was observed that at greater pit depths, sufficient
surrounding material was removed from the lamellae to form small fibres of uniform diameter. For the beryllium (1010) single crystal pits, the surface of the pit walls was normal to the [0001] and [1210] directions, while for the (1120) crystal surface, the lamellae were normal to the [0001] and [1100]. Examination of the (0001) showed the same effects as previously observed, the surface lacked any crystallographic orientation although pit propagation was often in the <1010> and <1120> families of directions. In the case of polycrystalline material from Figure 2.21, small fibres of unattacked beryllium were observed in the interior of the pit.

Figure 2.22 SEM micrographs of corrosion pits with parallel lamella of unattacked beryllium in single crystals surfaces: (a) (1010) and (b) (1120) [28].

2.13 Effect of corrosion on the mechanical properties of beryllium

Early investigations into the effect of corrosion on the mechanical properties of beryllium focused on forged beryllium. Concern surrounded the possibility that residual stresses from the forging may have been large enough to cause stress corrosion cracking (SCC) within beryllium components. SCC is a phenomenon whereby the combination of an applied stress and a particular corrosive environment leads to the formation of a crack that would not have been formed as a result of exposure to either one constraint individually [13]. It is a considerable problem, as material failure by SCC tends to be unexpected and rapid. The stresses can be a result of load in service or residual from manufacturing.

Forged samples were annealed at 750 °C for 20 minutes and an external load of 80% of the yield strength was applied inside a stress corrosion jig [32]. The samples were exposed to a 5 wt.% NaCl solution for 10 minutes and then dried in air for 50 minutes and the load cycle was repeated 500 times. The sample was electrically isolated from the holding grips to avoid galvanic effects. The samples failed in ~50 hours the pits formed during the test had penetrated up to 45 μm in depth and were found to initiate failure. The application of stress did not appear to have an effect on the formation rate of pits as unstressed tensile rods exposed to the same tests developed pits of the same size in the same time. Samples with protective coatings which were also exposed to the same tests did not appear to fail within 500 hours but did show signs of pitting [32].
Many stress corrosion tests have been performed on beryllium in numerous corrosive environments, with sustained stress levels of up to 90% of the yield stress. However, beryllium does not appear to be susceptible to SCC in any of the environments tested. The results from an extensive study are shown in Table 2.6. These solutions were chosen as they are known to induce stress corrosion cracking in other metals.

Table 2.6 Results of stressed beryllium samples to examine for SCC [32]

<table>
<thead>
<tr>
<th>Solution composition</th>
<th>pH</th>
<th>SCC</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 g L⁻¹ potassium chromate, 35 g L⁻¹ sodium chloride</td>
<td>8.4</td>
<td>No</td>
<td>General attack immediately</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pitting in 120 hours</td>
</tr>
<tr>
<td>20 g L⁻¹ potassium chromate, 35 g L⁻¹ sodium chloride</td>
<td>2.0</td>
<td>No</td>
<td>General attack accelerated</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pitting in 48 hours</td>
</tr>
<tr>
<td>20 g L⁻¹ potassium chromate, 35 g L⁻¹ sodium chloride</td>
<td>10.5</td>
<td>No</td>
<td>Rate of general attack decreased</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 g L⁻¹ potassium chromate, 35 g L⁻¹ sodium chloride</td>
<td>8.4</td>
<td>No</td>
<td>Immediate general attack and pitting</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>57 g L⁻¹ sodium chloride, 3 g L⁻¹ hydrogen peroxide</td>
<td>5.3</td>
<td>No</td>
<td>Immediate general attack</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Deep pits in 1 week</td>
</tr>
<tr>
<td>53 g L⁻¹ sodium chloride, 50 g L⁻¹ sodium chromate</td>
<td>2.0</td>
<td>No</td>
<td>Immediate general attack</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pitting after 200 hours</td>
</tr>
<tr>
<td>53 g L⁻¹ sodium chloride, 50 g L⁻¹ sodium chromate</td>
<td>11.0</td>
<td>No</td>
<td>No corrosion 1 month</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>36 g L⁻¹ chromic acid, 3 g L⁻¹ sodium chloride, 30 g L⁻¹ potassium dichromate</td>
<td>1.0</td>
<td>No</td>
<td>Severe pitting immediately</td>
</tr>
<tr>
<td>10 g L⁻¹ potassium fluoride</td>
<td>5.5</td>
<td>No</td>
<td>Immediate general attack</td>
</tr>
<tr>
<td>10 g L⁻¹ potassium fluoride</td>
<td>8.0</td>
<td>No</td>
<td>Immediate general attack</td>
</tr>
<tr>
<td>10 g L⁻¹ potassium fluoride</td>
<td>11.0</td>
<td>No</td>
<td>Slight attack</td>
</tr>
<tr>
<td>1% sulphuric acid</td>
<td>1.0</td>
<td>No</td>
<td>General surface attack</td>
</tr>
<tr>
<td>100 g L⁻¹ ferric chloride</td>
<td>2.0</td>
<td>No</td>
<td>Severe general corrosion - iron deposition on beryllium</td>
</tr>
<tr>
<td>100 g L⁻¹ cupric sulphate</td>
<td>4.0</td>
<td>No</td>
<td>Immediate general corrosion copper deposition on beryllium</td>
</tr>
<tr>
<td>100 g L⁻¹ magnesium chloride</td>
<td>4.3</td>
<td>No</td>
<td>Immediate general corrosion</td>
</tr>
<tr>
<td>100 g L⁻¹ sodium metasilicate</td>
<td>11.5</td>
<td>No</td>
<td>No corrosion in 7 days</td>
</tr>
</tbody>
</table>

An indication that an applied stress had a negative impact on the corrosion resistance of beryllium was reported for bare pickled beryllium and anodised beryllium [32]. In tests, both samples failed prematurely at applied stresses below the yield strength when exposed to sea water. The average time to failure for bare beryllium was 490 hours at 138 MPa and 305 hours at 207 MPa. For unstressed beryllium, the yield strength was found to be 380 MPa, the time to failure for anodised beryllium was ~360 hours at both stresses. Further studies showed that the time to failure decreased from 2350 hours to 40 hours as the applied stress increased from 8 MPa to 276 MPa. The samples tested were 98.3 at.% Be, 1.6 at.% BeO, 1.52 mm thick sheet that was polished and pickled prior to immersion in synthetic seawater. Failure occurred in the direction normal to the applied stress and was transgranular [32]. It is believed that although an applied stress accelerates corrosion, the pit density of stressed samples was no different to that observed on unloaded samples. Instead of increased pitting, it was concluded that one or more pits were more severe, penetrating further into the metal than other pits, resulting in failure.
From these various investigations it was concluded that failure did not occur as a result of SCC but as a result of:

- increased stress concentration at corrosion pits
- decreased cross sectional area

More recently the effect of pitting corrosion in varying concentrations of NaCl, on the mechanical properties of S-200F beryllium has been investigated [31]. The mechanical strength of samples was assessed using a four point bend test. The samples were 25 mm long, 5 mm wide and 2.5 mm thick. Each face was polished to a 400 grit finish. Samples were mounted to achieve uniform exposure to the aqueous environment and isolated from galvanic effects by bonding the smallest face to an alumina stand.

Samples were immersed in aerated NaCl solutions with concentrations of 1 M, 0.1 M and 0.01 M for 168 hours. Ten samples were tested at each concentration. Four point bend tests were carried out on each sample. Figure 2.23 shows the bending stress-displacement plots obtained for as-received and the samples exposed to different concentrations of NaCl. Both the strain and the ultimate tensile strength were affected while the yield strength did not seem to be affected by exposure to the corrosive media. It is interesting to note that the sample exposed to the greatest concentration of NaCl was not the most adversely affected sample. While the lowest tensile strength was obtained for the 0.1 M solution sample and the highest tensile strength was obtained for the 1 M sample [31].

![Figure 2.23 Representative bending stress-displacement plot for beryllium samples exposed to various NaCl concentrations for 168 hours [31].](image)

SEM micrographs of the samples showed significant differences in the pitting morphology. Exposure to the 1 M solution showed the greatest number of pits, each being 1-3 μm deep and spaced ~15 μm apart. Exposure to the 0.01 M solution showed fewer deeper pits, each being 5-20 μm deep and spaced ~250 μm apart. This was in agreement with optical microscopy which showed that the sample exposed to the 1 M solution was more generally corroded while the sample exposed to the 0.01 M solution showed significant differences in topography from one area to the next. This was also supported by AFM measurements. These showed a root mean square surface roughness of 16 nm and 14 nm respectively for the 0.01 and 1 M solutions and 6 nm for the as-received surface. The AFM profiles highlighted the different contributions to
the surface roughness. For the sample exposed to the 1 M solution, uniform roughness was recorded but the 0.01 M solution sample showed isolated large spikes in roughness [31].

The changes observed in the pitting morphology explained the unexpected results from the four point bend tests. The beryllium showed more uniform corrosion and decreased pitting as the NaCl concentration was increased. When pits are considered as material flaws and regions of stress concentration, it is logical that the deepest pits result in the highest stress concentrations and thus yield the greatest degradation in the mechanical properties. It was also concluded that it is not the degree of surface pitting but the pit morphology that is most important in determining the mechanical properties of beryllium components in corrosive environments [31].

Building upon the results obtained on beryllium fracture in different chloride concentrations an investigation focused on examining the possibility of microbiologically induced corrosion. Microbiological corrosion is observed for a number of metals and is known to negatively affect their mechanical properties [33]. The investigation was performed on S-200F beryllium using the same four point bend test as the previously mentioned study. An aerobic bacterial strain Pseudomonas species NCMB 2021 was used. The bacteria were grown in 1 M NaCl solution containing 1.5 g L⁻¹ yeast extract and 1 g L⁻¹ dextrose. Bend tests were performed on samples exposed for 168 hours to the solution containing bacteria and a solution of 1 M NaCl with no bacteria. Solutions were kept at 22 °C. As part of the investigation samples coated with a monolayer of silane, designed to act as a protective layer, were also added to the 1 M NaCl solution with bacteria. Figure 2.24 shows the results obtained from the investigation. In line with the results obtained in the previous investigation the samples exposed to the 1 M solution without bacteria did not show a large difference in ultimate tensile strength, a drop of only 3% compared to the as-machined surface. The sample exposed to the solution containing bacteria showed a much greater degradation in mechanical properties, with a 23% drop in tensile strength compared to the as-machined sample [34].

![Figure 2.24](image-url)

**Figure 2.24** Representative bending stress-displacement plot for beryllium samples exposed to control and bacteria containing 1 M NaCl solutions [34].

The changes in the mechanical properties were again linked to the difference in the pitting morphology. Exposure of the beryllium samples to the bacteria containing solution resulted in the formation of biofilm
growths on the surface that led to deep non-uniform pitting. These pits acted as stress concentrations, initiating cracking. Exposure to the solution free of bacteria resulted in generalised attack of the surface with small, shallow pits. Samples coated with a protective monolayer of silane showed similar behaviour to the samples exposed to the solution free of bacteria, exhibiting a uniform distribution of small shallow pits. It was concluded that the silane prevented formation of biofilms and the associated heavy pitting but not the general uniform pitting from the NaCl solution [34].

2.14 Beryllium packaging materials

While much work has been carried out focusing on the corrosion of beryllium in aqueous environments, containing various concentrations of chlorine, there is little literature describing the potential effects of residual cleaning or processing solutions left behind on components or contaminants introduced during storage. Two studies have focused on Celotex [27,35] and two further studies have focused on the interaction of chlorinated solvents on the surface of beryllium [5,36]. Celotex is a sugarcane fibre that is a commonly used packing material in storage containers for beryllium components. It is composed of ~95 wt.% cellulose and ~5 wt.% starch. In addition to the organic components it contains trace amounts of inorganic constituents.

EDX has been used as well as ion chromatographic analysis (ICA) to determine the amount of chlorine present in various Celotex samples. Energy dispersive x-ray spectroscopy (EDX) was performed on three samples in five different areas and an average taken over the five areas to determine the wt.% of a range of elements in each. While sulphate ions are also known to cause corrosion, the sulphur content was not subject of the investigation [10]. However, the concentration of sulphur in the samples was recorded. Table 2.7 shows the average concentrations of sulphur and chlorine from the three Celotex samples [35].

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample 1</td>
</tr>
<tr>
<td>Cl</td>
<td>3.82</td>
</tr>
<tr>
<td>S</td>
<td>3.97</td>
</tr>
</tbody>
</table>

The quantification was normalised to 100% for all the elements in the EDX analyses. The actual wt.% of chlorine and sulphur is much lower than those shown in the tables because Celotex contains <5% inorganic constituents with the remaining 95% organic. ICA was also performed which showed amounts of chloride and sulphide as 0.96 g kg\(^{-1}\) and 1.6 g kg\(^{-1}\) of Celotex respectively. It is also noted that that trace amounts of bromine and fluorine were also detected at concentrations of 0.05 g kg\(^{-1}\) and 0.009 g kg\(^{-1}\) Celotex respectively [35].

ICA performed by Lawrence Livermore National Laboratory (LLNL) on a sample of Celotex provided a similar concentration of chlorine, which was 0.94 g kg\(^{-1}\) of Celotex. Fluorine was also found to be present at 0.125 g kg\(^{-1}\). Further analysis, by Los Alamos National Laboratory (LANL), on a larger sample of 20 lbs (9.1 kg) of Celotex, showed a chlorine concentration of 1.79 g kg\(^{-1}\) and a fluorine concentration of 0.9 g kg\(^{-1}\) of Celotex [27]. The difference in the amounts obtained by the different laboratories was believed to be a
consequence of the extraction procedures and immersion times employed to remove the chlorine from the Celotex.

To investigate the influence of chloride originating from Celotex packaging on the surface of beryllium, carbon tetrachloride (CCl₄) was chosen to simulate the reaction between BeO and chlorine. Thermodynamic calculations indicated that the chlorine in CCl₄ was able to react with BeO to form BeCl₂; it was therefore deemed that the chlorine present in Celotex was able to lead to beryllium corrosion [5]. This was supported by later experimental work [36].

The results from both the investigation into the packaging material and the cleaning solvents used on beryllium indicated that traditional storage conditions which expose beryllium to Celotex and moisture will result in pitting corrosion of the beryllium.

2.15 Effects of chlorinated solvents on the beryllium surface

Following the discovery of pitting corrosion caused by chlorine originating from the packaging material used with beryllium components, other possible sources of contamination began to be investigated. One route believed to be a possible source of chlorine was cleaning solvents. Chlorinated solvents are traditionally used to degrease finished metal components, in order to remove various soils. An investigation was performed in order to assess the amount of residual chlorine left on beryllium surfaces after exposure to three commonly used chlorinated solvents. Focus was also given to the effect of this chlorine on the beryllium at near ambient conditions [36].

The study was performed using S-200D beryllium coupons obtained from LLNL. The coupons were prepared by polishing under deionised, distilled (DDI) water followed by ultrasonic cleaning in DDI water. The coupons were allowed to air dry for four hours to form their native oxide. The three chlorinated solvents used for vapour degreasing of the beryllium in the study are shown in Table 2.8. The table includes the supplier, grade and the additives present in the solvents.

Trichloroethane (TCA) contains additives called inhibitors. These perform a number of functions including: adsorption of UV light, scavenging of acid and preventing reaction of the solvent with the metal. Trichloroethene (TCE) also contains these but only at a trace concentration. The inhibitors typically include:

- Nitromethane - absorbs UV photons, preventing photo degradation of solvent molecules
- Butylene dioxide - reacts with acids to form alcohols
- Dioxolane - promotes the formation of surface oxide at exposed metal surfaces

The cleaned air-dried beryllium coupons were vapour degreased at 50 °C and exposed to the vapours of either TCA or TCE. The treated samples were then analysed by XPS. Further to this, two water polished coupons were polished again under either TCA or CCl₄ to examine if the bare beryllium metal would react with the chlorinated solvent. This was also expanded to include scraping and scratching two samples.
submerged in TCA. Finally coupons degreased in TCA were rinsed with copious amounts of DDI water followed by a light wipe with a DDI soaked scientific cleaning wipe and analysed by XPS.

Table 2.8 Breakdown of information from chlorinated solvents traditionally used to degrease beryllium components

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Supplier</th>
<th>Grade</th>
<th>Impurities/additives</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,1,1-Trichloroethane</td>
<td>American Chemical Enterprises, Inc.</td>
<td>Technical</td>
<td>≥90% TCA by volume ≥2% all other halogens by volume</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Inhibitors 100 ppm H₂O max</td>
</tr>
<tr>
<td>1,1,2-Trichloroethene</td>
<td>Burdick &amp; Jackson Laboratories, Inc.</td>
<td>Reagent grade</td>
<td>0.006% KF H₂O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.28 ppm Inhibitors</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>Matheson, Coleman &amp; Bell</td>
<td>Spectroquality grade</td>
<td>+99% CCl₄ 0.03% H₂O max</td>
</tr>
</tbody>
</table>

Figure 2.25 shows the high resolution Cl 2p spectrum from a beryllium sample polished using DDI water. Figure 2.26 (a) shows the high resolution Cl 2p spectrum from a beryllium sample polished was DDI polished followed by vapour degreasing in TCA and (b) was polished using DDI and then vapour degreased in TCE. In each case, the broad Cl 2p peak was fitted to show two sets of doublets. The Cl 2pₓ/₂ - 2p₁/₂ doublet is separated by 1.6 eV and has a peak area ratio of 2:1. Two sets of peaks are observed because splitting occurs for the organic carbon-bonded chlorine and the inorganic chloride at the surface. The splitting indicates that the TCA and TCE vapours reacted with beryllium metal and that solvent residue remained on the surface [36].
By scraping the surface of beryllium, while submerged in TCA, the protective oxide was removed and bare metal was directly exposed to the chlorinated solvent. Analysis of the scraped metal surface without rinsing with water showed a trace of organic chlorine and a large amount of inorganic chloride, as shown by the large chloride peak in Figure 2.27 (a). Another sample was scraped while submerged but before analysis was rinsed in DDI water and then wiped with a damp tissue. The spectrum collected from this sample is shown in Figure 2.27 (b). Comparison of the scraped sample to the rinsed sample showed a large reduction in inorganic chlorine. The results indicate that the free beryllium surface reacts with the chlorinated solvent. Quantification showed a reduction in the chloride concentration by more than 80% after rinsing because beryllium chloride is highly soluble in water [37].

Comparison of the XPS data of all the samples in the study is shown in Table 2.9. The data highlighted two aspects:

1. Samples vapour degreased with TCE retained a greater surface chloride concentration than those degreased with TCA.

2. Washing TCA cleaned samples removed a significant amount of surface inorganic chloride.
In this study thermodynamic calculations were used to support the theory of inorganic chloride formation [36]. Two possible reactions were proposed: the first on exposed bare beryllium Equation 2.7, the second on passivated beryllium Equation 2.8.

$$\text{Be-Be + C-Cl} \rightarrow \text{Be-C + Be-Cl} \quad (2.7)$$

$$\text{Be-O + C-Cl} \rightarrow \text{Be-Cl + C-O} \quad (2.8)$$

Of the two reactions the first is thermodynamically more favourable at room temperature with a negative enthalpy of reaction $\Delta H_r = -152 \text{ kcal (636 kJ) mol}^{-1}$. The second reaction has a positive enthalpy of reaction $\Delta H_r = 10.9 \text{ kcal (45.6 kJ) mol}^{-1}$. It is therefore less likely that chlorinated solvent will react with passivated beryllium to produce inorganic chloride. The results of this study revealed that to minimise the potential for corrosion, vapour degreased components should be: rinsed with copious amounts of DDI water followed by a light wipe with a DDI soaked scientific cleaning wipe.

Thermodynamic calculations in a previous study [5] based upon how two chlorinated solvents will react with a passive beryllium surface are not fully consistent with experimental XPS data shown for the same chlorinated degreasing solvents [36].

The potential for TCA and TCE to cause corrosion on beryllium was modelled using Thermo-Calc. Property diagrams can be generated in this programme to model various interactions of reagents based on thermodynamic properties and phase diagrams. The property diagrams modelled the interactions in a system containing BeO, CO$_2$, O$_2$, H$_2$O and the given solvent at room temperature and pressure. The results of the modelling indicated that beryllium chloride was produced when passivated beryllium was exposed to TCE but not when exposed to TCA [5]. While this is supported by the thermodynamics and Equation 2.8 which shows a positive enthalpy of reaction $\Delta H_r = 10.9 \text{ kcal (45.6 kJ) mol}^{-1}$, experimentally it was shown that TCA is able to react with a beryllium oxide surface as shown by the inorganic chloride peaks in Figure 2.26. However, the amount of chloride was significantly lower than that of a sample exposed to TCE.

The results of the calculations suggested that the H:Cl ratio in the solvent molecule played an important role in the ability of the solvent to react with beryllium oxide. The thermodynamic calculations were repeated for twenty different chlorinated solvents with H:Cl ratios of 0 - 5, the results are shown in Table 2.10.
The results of the study suggested two requirements in order for a solvent to react with beryllium, these were:

1. Carbon is essential to form beryllium chloride from beryllium oxide
2. The H:Cl ratio must be less than 1 in the solvent molecule

With an H:Cl ratio greater than one, no beryllium chloride is formed and instead the more thermodynamically stable hydrochloric acid is formed [5].

Table 2.10 Results of thermodynamic calculations to predicting the formation of BeCl$_2$ on beryllium from various solvents [5]

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Formula</th>
<th>BeCl$_2$ Product</th>
<th>H:Cl ratio</th>
<th>C in the solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon tetrachloride</td>
<td>CCl$_4$</td>
<td>Yes</td>
<td>0/4</td>
<td>1</td>
</tr>
<tr>
<td>Chloroform</td>
<td>CCl$_3$H</td>
<td>Yes</td>
<td>1/3</td>
<td>1</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>CCl$_2$H$_2$</td>
<td>No</td>
<td>2/2</td>
<td>1</td>
</tr>
<tr>
<td>Chloromethane</td>
<td>CCIH$_3$</td>
<td>No</td>
<td>3/1</td>
<td>1</td>
</tr>
<tr>
<td>Tetrachloroethene</td>
<td>C$_2$Cl$_4$</td>
<td>Yes</td>
<td>0/4</td>
<td>2</td>
</tr>
<tr>
<td>Trichloroethene (TCE)</td>
<td>C$_2$Cl$_3$H</td>
<td>Yes</td>
<td>1/3</td>
<td>2</td>
</tr>
<tr>
<td>Dichloroethene</td>
<td>C$_2$Cl$_2$H$_2$</td>
<td>No</td>
<td>2/2</td>
<td>2</td>
</tr>
<tr>
<td>Chloroethene</td>
<td>C$_2$ClH$_3$</td>
<td>No</td>
<td>3/1</td>
<td>2</td>
</tr>
<tr>
<td>Hexachloroethane</td>
<td>C$_6$Cl$_6$</td>
<td>Yes</td>
<td>0/6</td>
<td>2</td>
</tr>
<tr>
<td>Pentachloroethane</td>
<td>C$_5$Cl$_5$H</td>
<td>Yes</td>
<td>1/5</td>
<td>2</td>
</tr>
<tr>
<td>Tetrachloroethane</td>
<td>C$_5$Cl$_4$H$_2$</td>
<td>Yes</td>
<td>2/4</td>
<td>2</td>
</tr>
<tr>
<td>Trichloroethene (TCA)</td>
<td>C$_5$Cl$_3$H$_3$</td>
<td>No</td>
<td>3/3</td>
<td>2</td>
</tr>
<tr>
<td>Dichloroethene</td>
<td>C$_5$Cl$_2$H$_4$</td>
<td>No</td>
<td>4/2</td>
<td>2</td>
</tr>
<tr>
<td>Chloroethene</td>
<td>C$_5$ClH$_5$</td>
<td>No</td>
<td>5/1</td>
<td>2</td>
</tr>
<tr>
<td>Hexachlorobenzene</td>
<td>C$_6$Cl$_6$</td>
<td>Yes</td>
<td>0/6</td>
<td>6</td>
</tr>
<tr>
<td>Pentachlorobenzene</td>
<td>C$_6$Cl$_5$H</td>
<td>Yes</td>
<td>1/5</td>
<td>6</td>
</tr>
<tr>
<td>Tetrachlorobenzene</td>
<td>C$_5$Cl$_4$H$_2$</td>
<td>Yes</td>
<td>2/4</td>
<td>6</td>
</tr>
<tr>
<td>Trichlorobenzene</td>
<td>C$_6$Cl$_3$H$_3$</td>
<td>No</td>
<td>3/3</td>
<td>6</td>
</tr>
<tr>
<td>Dichlorobenzene</td>
<td>C$_6$Cl$_2$H$_4$</td>
<td>No</td>
<td>4/2</td>
<td>6</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>C$_6$ClH$_5$</td>
<td>No</td>
<td>5/1</td>
<td>6</td>
</tr>
</tbody>
</table>

The conclusions of this investigation suggested that TCE cleaning solvent should be replaced with a lower carbon containing, higher H:Cl solvent such as: chloromethane or dichloromethane. However, further experimental evidence would also be needed to prove the conclusions of the investigation, as it is important to note that the phase diagram only takes into account the thermodynamics of the selected reactions and not the kinetics [5,35].

2.16 Second phase particles

2.16.1 Impurities in beryllium

A wide range of commercial grades of beryllium are available, Table 2.11 lists the composition of each these grades. While this table shows the main grades of beryllium that are available, it only represents compositions within the public domain. As such, other grades are available and have been used in investigations described in this review but their compositions are unknown. It also only represents modern day beryllium. Much of the beryllium used in the corrosion studies from the early literature contained unknown quantities of impurities but undoubtedly contained a greater concentration of impurities.
Materion Brush uses three designations for beryllium grades depending upon the intended use of the metal. Structural grades are designated "S" and are produced using vacuum hot isostatic pressing. It is formed by heating beryllium powder under pressure which results in a uniform almost fully dense, fine-grained beryllium component. Instrument grade beryllium is designated "I" and it is produced by hot isostatic pressing for applications where a high micro yield is required. Optical grade beryllium is designated "O", although other grades of I and S are also included. It is also produced by hot isostatic pressing. It has highest isotropy of thermal and mechanical properties of any grade of beryllium and is best suited for cryogenic applications [38]. S-65 grade beryllium was used in all of the experimental work in this thesis. It has the lowest level of metallic impurities for any structural grade of beryllium making it compatible with nuclear energy and reactor applications. In these structural grades, the ratio of iron to aluminium is carefully controlled the reasons for this will be discussed in a later section.

Table 2.11 Chemical composition of commercially available grades of beryllium [38]

<table>
<thead>
<tr>
<th>Grade</th>
<th>Chemical composition (at.% max)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Be % min BeO Al C Fe Mg Si Other*</td>
</tr>
<tr>
<td>I-70H</td>
<td>99.0 0.7 0.07 0.07 0.10 0.07 0.07 0.04</td>
</tr>
<tr>
<td>I-220H</td>
<td>98.0 2.2 0.10 0.15 0.15 0.08 0.08 0.04</td>
</tr>
<tr>
<td>O-30H</td>
<td>99.0 0.5 0.07 0.07 0.12 0.12 0.07 0.04</td>
</tr>
<tr>
<td>S-65</td>
<td>99.2 0.9 0.05 0.09 0.08 0.01 0.045 0.045</td>
</tr>
<tr>
<td>S-200F</td>
<td>98.5 1.5 0.10 0.15 0.13 0.13 0.08 0.04</td>
</tr>
<tr>
<td>S-200FH</td>
<td>98.5 1.5 0.10 0.15 0.13 0.08 0.08 0.04</td>
</tr>
<tr>
<td>SR-200</td>
<td>98.0 2.0 0.16 0.15 0.18 0.08 0.08 0.04</td>
</tr>
<tr>
<td>S-200D</td>
<td>98.0 2.0 0.16 0.15 0.13 0.18 0.08 0.04</td>
</tr>
</tbody>
</table>

*Varying concentrations of Cr, Ni, Cu, Ti, Zn, Mn, Ag, Pb, Ca, Mo, U.

Beryllium under normal conditions is usually highly resistant to corrosion and is able to remain bright for years in service under normal conditions [11]. The excellent corrosion behaviour is a consequence of the adherent protective oxide formed on the surface this film is uniform, nearly non-porous and very thin. The metal forms an oxide film up to 3 nm thick within two hours of exposure to air at room temperature. Because of the oxide layer, beryllium, that is clean, free of surface impurities and inclusions has exceedingly good corrosion resistance in high purity water, with corrosion rates typically < 25 μm year⁻¹ [32,39].

Understanding the nature of second phase particles is crucial to providing an insight into pitting corrosion processes affecting many metals and their alloys. These include: aluminium, beryllium, copper, stainless steels and zinc. All of these metals are prone to pitting corrosion because of their inherent passivity provided by thin surface oxide layers.

2.16.2 Beryllium carbide inclusions

The nature and behaviour of corrosion caused by carbide inclusions was understood relatively early on in the history of beryllium pitting corrosion research. The beryllium carbides undergo hydrolysis in the presence of a humid environment when they are exposed at the metal surface by machining.

One of the earliest studies on second phase inclusions was based upon the observation of scientists at Oak Ridge National Lab in 1947 [10]. Corrosion had occurred on several pieces of unknown purity beryllium...
which was extruded and machined in air. These pieces were exposed to the local atmosphere for approximately 6 months. During the experiment the beryllium was exposed to various temperatures and a number of high humidity days. During this time, deposits of white flaky corrosion products began to form. These deposits were orientated parallel to the extrusion axis of the beryllium. The white corrosion products were examined by XRD and found to be a mixture of hydrated beryllium oxide, BeO.xH₂O and/or beryllium hydroxide, Be(OH)₂. It was later discovered that the formation of blisters and white corrosion products on the surface was caused by the hydrolysis of beryllium carbide inclusions [10]. This type of corrosion has been duplicated with carbide seeded beryllium [12].

Any beryllium carbide particles exposed at the metal surface, as a result of machining, are susceptible to hydrolysis. Moisture in the environment is able to slowly react with the carbide and form beryllium oxide or beryllium hydroxide corrosion products. Methane gas is also produced as a result of Equations 2.9 or 2.10.

\[
Be_2C + 2H_2O \rightarrow 2BeO + CH_4 \quad (2.9) \\
Be_2C + 4H_2O \rightarrow 2Be(OH)_2 + CH_4 \quad (2.10)
\]

The hydrated beryllium oxides occupy a volume approximately four times greater than that of the carbide. The result is significant volume expansion and the formation of large blisters on the beryllium surface around the carbide inclusion. This can cause precision components to be scrapped because of the disruption to their finely machined surface [12].

Carbide inclusions are present in most commercially available beryllium. Carbon concentrations typically range from 700-1500 ppm, as shown in Table 2.11. Beryllium carbide inclusions can be evenly distributed as fine particles or as a few larger particles. The difference in their distribution leads to variations in the beryllium corrosion behaviour. One particularly interesting study examined the effect of an unusually large carbide inclusion present in a precision beryllium component [11]. The pocket of material containing the inclusion was ruptured during machining exposing part of the carbide at the surface. During storage this reacted as per Equations 2.9 and 2.10 leading to volume expansion and fracture around the inclusion. This led to a large section of beryllium breaking away from the component. While the chances of an inclusion of this size occurring in modern beryllium are exceedingly low it makes an interesting study. The component is shown in Figure 2.28.
2.16.3 Iron-beryllium intermetallics

The earliest work on the identification of beryllium intermetallics originates in the 1920s and 1930s. This research helped to provide the experimental results for the early beryllium binary phase diagrams of: Be-Al, Be-Cu, Be-Co, Be-Fe and Be-Ni [40]. Iron is one of the primary impurities in structural grades of beryllium. As such, an important binary system is Be-Fe. Whilst work to identify beryllium intermetallics was being performed in early research, the link between these phases and corrosion is still ongoing.

The first intermetallic phases identified in the Be-Fe system were Fe$_2$Be and Fe$_5$Be. These compounds were discovered by x-ray and magnetic investigations of beryllium second phase particles. The Fe$_2$Be intermetallic was found to contain 12 atoms per unit cell, be hexagonal close packed, had lattice parameters of $a = 4.212$ Å and $c = 6.845$ Å and a density of 4.65 g cm$^{-3}$. The Fe$_5$Be intermetallic was found to contain 24 atoms per unit cell, have a face centred cubic structure, had a lattice parameter of $a = 5.878$ Å and a density of 3.17 g cm$^{-3}$ [41]. The presence and structure of these iron beryllides has subsequently been confirmed by another investigation [42]. Examination of XRD data from various Be-Fe alloys estimated the composition of a phase to be 7.8 - 8.3 at.% iron which corresponded to an iron intermetallic with the formula FeBe$_{11}$. The FeBe$_{11}$ structure was found to contain 18 atoms per unit cell, was hexagonal close packed, had lattice parameters of $a = 4.130$ Å and $c = 10.424$ Å and a density of 2.50 g cm$^{-3}$ [42]. The authors noted that FeBe$_2$ had a melting point of 1480 °C while FeBe$_5$ and FeBe$_{11}$ had much lower melting points. The results of this investigation into the phases present in the Be-Fe system are shown in Table 2.12.

Table 2.12 Characterisation data on the solid phases present in the Be-Fe system

<table>
<thead>
<tr>
<th>Formula</th>
<th>Lattice structure</th>
<th>Atoms per unit cell</th>
<th>Lattice dimensions (Å)</th>
<th>Density (g cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>HCP</td>
<td>2</td>
<td>2.281 3.577</td>
<td>1.841</td>
</tr>
<tr>
<td>FeBe$_{11}$</td>
<td>HCP</td>
<td>18</td>
<td>4.130 10.424</td>
<td>2.474</td>
</tr>
<tr>
<td>FeBe$_5$</td>
<td>FCC</td>
<td>24</td>
<td>5.884</td>
<td>3.241</td>
</tr>
<tr>
<td>FeBe$_2$</td>
<td>HCP</td>
<td>12</td>
<td>4.212 6.853</td>
<td>4.572</td>
</tr>
<tr>
<td>$\alpha$-Fe</td>
<td>FCC</td>
<td>2</td>
<td>2.861</td>
<td>7.871</td>
</tr>
</tbody>
</table>

There has been much discussion as to the true formula for the proposed compound FeBe$_{11}$ and whether it was actually FeBe$_{12}$, a body centred tetragonal crystal structure, with lattice parameters $a = 7.253$ Å and $c = 4.232$ Å. An attempt was made to produce the compound FeBe$_{12}$ by melting iron and beryllium mixtures of
approximately 1:15, Fe:Be atomic ratio in a tungsten arc furnace, under a helium atmosphere [43]. The density of the FeBe_{11} and FeBe_{12} compounds were found to be 2.47 g cm\(^{-3}\) and 2.45 g cm\(^{-3}\) respectively and so it was initially assumed that the two compounds were the same. Correspondence between authors established that both structures did exist but that FeBe_{11} was the compound present in beryllium [25].

A later investigation confirmed the presence of FeBe_{11} and FeBe_{5} in beryllium [44]. It was found that high concentrations of FeBe_{5} could be produced from a 5 wt.% iron alloy heated to above 1000 °C and then quenched. XRD confirmed the structure. XRD of the alloys produced by heat treatment in the range 600-1000 °C confirmed the presence of a hexagonal structure with the formula FeBe_{11} and not the tetragonal structure of FeBe_{12}.

Another Be-Fe intermetallic is thought to occur in beryllium. BeFe\(_3\) forms a cubic close packed structure with a lattice parameter of 5.61 Å. It is thought to be a metastable phase found during aging [45,46]. Figure 2.29 shows the Be-Fe phase diagram with the three common intermetallic phases shown as \(\varepsilon\) at 9 - 11 at.% iron, \(\delta\) at 7 - 18 at.% iron and \(\zeta\) at 21 - 37 at.% iron. The phase diagram was produced using CalPhad. It represents the most complete understanding of the Be-Fe binary system to date and matches very well with experimentally derived binary phase diagrams drawn in the past [40,42,47].

![Figure 2.29 Binary phase diagram for the Be-Fe system. The composition ranges for the three common iron intermetallics present in beryllium \(\varepsilon\)-FeBe_{11}, \(\delta\)-FeBe_{5} and \(\zeta\)-FeBe_{2};[46].](image)

Following on from the early research into the Be-Fe system, it is now generally agreed that the iron beryllides formed in beryllium are: the \(\varepsilon\)-phase FeBe_{11}, the \(\delta\)-phase FeBe_{5} and the \(\zeta\)-phase FeBe_{2}. It is understood that the FeBe_{11} phase can be formed from the monotectoid transformation of FeBe_{5} by heat treatment [48,49].
An analytical study of impurity phases in beryllium found that beryllium oxide, beryllium carbide, free silicon and at least two intermetallic phases were identified. X-ray diffraction of beryllium containing deliberate additions of 1 wt.% iron and 1 wt.% aluminium showed the presence of a crystal structure analogous to the cubic close packed structure of FeBe$_5$ having a lattice parameter of $a = 6.057$ Å compared to $a = 5.88$ Å for FeBe$_5$ and so the phase was denoted Be$_5$Y [44]. The increase in the measured lattice parameter was believed to be a consequence of the aluminium present in solid solution. The designation was therefore changed to ($\text{Fe,Al}$)Be$_5$. It was confirmed that heat treatment and subsequent aging produced the phase in beryllium, with reprecipitation occurring by subsequent heat treatment in the temperature range 600 - 800 °C.

The ternary phase ($\text{Fe,Al}$)Be$_5$ was refined through independent work carried out at the same time [50]. The aim of this work was to identify possible AlMBe$_4$ phases present in beryllium. A number of compositions were prepared, consisting of aluminium and beryllium with the addition of manganese, nickel, iron or chromium. Alloys were prepared by heating the desired compositions of powders in vacuum until equilibrium was believed to have been reached. The products of the reactions were then ground and analysed by XRD. Single face centred cubic phases were observed in the manganese, nickel and iron systems. The measured lattice parameters were found to be 6.11 Å, 6.01 Å and 6.06 Å respectively [50]. The measured lattice parameter for AlFeBe$_4$, 6.06 Å, matched that of ($\text{Fe,Al}$)Be$_5$, 6.057 Å and so it was concluded this phase was the intermetallic AlFeBe$_4$. Given the results of this study it has been suggested that other transition metal impurities, if present, may also be able to form this or a similar phase in place of iron [25].

### 2.16.4 The AlFeBe$_4$ precipitate and the important role it plays in beryllium

Aluminium, silicon and magnesium are elements that are highly insoluble in beryllium [16]. As such, upon cooling, these elements are concentrated along grain boundaries in the metal. This can result in hot shortness - a loss of high temperature ductility. Aluminium is considered to be the main element responsible for this. The amount of free aluminium in beryllium can be reduced by adding iron, to form the precipitate AlFeBe$_4$. If the wt.% of iron added to beryllium is twice that of the aluminium wt.%, the precipitate can form when the iron reacts with and "mops up" the free aluminium. While it is important to maintain this 2:1 ratio of iron to aluminium it is also important to age beryllium at 600-850 °C to allow the added iron to diffuse to the grain boundaries and react with the aluminium. As the beryllium cools, the solubility of iron decreases and if the rate of cooling is too high the excess iron can precipitate as FeBe$_{11}$. A reaction scheme for this is shown in Figure 2.30.
Figure 2.30 Reaction scheme to highlight the various effects that occur in beryllium during aging. Upon cooling from ~850 °C, iron is able to precipitate in the matrix as FeBe$_{11}$, react with aluminium at grain boundaries or remain in the matrix as soluble iron [51].

Figure 2.31 shows the dramatic effect of the free aluminium concentration on the high temperature ductility of beryllium. With an increase in free aluminium from 200 - 300 ppm, the reduction in ductility is dramatic with a sudden decrease from 25 to 5% elongation. For the best performance, the concentration of free aluminium should be kept below 200 ppm. While it is important to add iron to beryllium in order to reduce the free aluminium content, it should not be added in too great an excess. If too much iron is precipitated as FeBe$_{11}$, beryllium has decreased fracture toughness [45].

Figure 2.31 Graph of the relationship between free aluminium concentration in beryllium and ductility at 566 °C [51].

2.16.5 Other beryllides

Although AlFeBe$_4$ is the most widely studied intermetallic, because it has been associated with pitting corrosion, many other beryllides are known to be present in commercial beryllium [12,23,49]. The presence of silicon, as detected by EDX and electron microprobe analysis (EMPA), has been associated with corrosion initiation sites [23]. An investigation, using transmission electron microscopy (TEM), of weld cracks in beryllium welds revealed the presence of nodules containing aluminium and silicon in addition to the intermetallic phases TiBe$_{12}$ and AlFeBe$_4$ at grain boundaries. These were also found to be present on the fracture surfaces of the weld cracks [52].

Work on the identification of the precipitate AlFeBe$_4$ initially suggested that as well as iron, many other transition metals could form this compound with aluminium and beryllium. Silicon, albeit with a much larger lattice parameter, was believed to be able to form this phase [25]. However, subsequent work carried out by the same author, attempting to substitute silicon into the compound met with failure and resulted in substantial quantities of elemental silicon in the beryllium samples [25].
There is currently no evidence in the literature suggesting the formation of a binary Be-Si intermetallic. An extensive list of the known beryllides is shown in Table 2.13 [16]. There is also no evidence for the formation of an Al$_x$Si$_y$Be$_z$ ternary phase based on examination of the latest ternary phase diagram for this system [53]. Although, based upon recent EDX analysis it has been shown that silicon is associated with titanium [23], suggesting a possible ternary phase or a binary phase with titanium. Titanium or Ti-Si based intermetallics have been identified in beryllium and associated with pitting corrosion, it is possible this is the intermetallic TiBe$_{12}$, which has been associated with fracture surfaces in beryllium welds as mentioned previously and has undergone investigation as part of corrosion studies [23,48].

Table 2.13 Known forms of beryllides (M = metal) [16]

<table>
<thead>
<tr>
<th>Phase</th>
<th>Crystal structure</th>
<th>Metals</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeBe</td>
<td>Cubic</td>
<td>Ti, Co, Ni, Cu, Pd</td>
</tr>
<tr>
<td></td>
<td>Cubic $T^4$</td>
<td>Au</td>
</tr>
<tr>
<td>MBe$_2$</td>
<td>FCC</td>
<td>Ti, Nb, Ag, Ta</td>
</tr>
<tr>
<td></td>
<td>Hexagonal $D^{6h}$</td>
<td>V, Cr, Mn, Fe, Mo, W, Re</td>
</tr>
<tr>
<td></td>
<td>Hexagonal $D^{16h}$</td>
<td>Zr, Hf</td>
</tr>
<tr>
<td>MBe$_3$</td>
<td>Cubic</td>
<td>Pd, Au</td>
</tr>
<tr>
<td></td>
<td>FCC</td>
<td>Fe</td>
</tr>
<tr>
<td></td>
<td>Hexagonal</td>
<td>Zr, Hf</td>
</tr>
<tr>
<td>$M_2$Be$_{17}$</td>
<td>Rhombohedral</td>
<td>Ti, Zr, Nb, Hf, Ta</td>
</tr>
<tr>
<td>MBe$_{12}$</td>
<td>Tetragonal</td>
<td>V, Cr, Nb, Mo, Ta, W</td>
</tr>
<tr>
<td></td>
<td>Hexagonal</td>
<td>Ti</td>
</tr>
<tr>
<td>MBe$_{13}$</td>
<td>FCC</td>
<td>Y, Zr, Hf, La, Ce, Th, U, Np, Pu, Am, Ca, Mg</td>
</tr>
<tr>
<td>MBe$_{22}$</td>
<td>FCC</td>
<td>Mo, W, Re</td>
</tr>
</tbody>
</table>

2.17 The role of beryllides in corrosion

Three beryllides have been extensively investigated for their possible involvement in the corrosion of beryllium, these were: FeBe$_5$, AlFeBe$_4$ and TiBe$_{12}$. While the concentration of titanium in commercial beryllium is usually below 400 ppm, it was included in the investigation as it had previously been observed at grain boundaries in weld cracking [52]. The three intermetallic compositions were produced by arc-melting stoichiometric amounts of the alloying elements. The composition of the produced pellets was checked using XRD. An example of the pattern collected from the AlFeBe$_4$ intermetallic is shown in Figure 2.32.
The XRD patterns for FeBe₅ and TiBe₁₂ showed single phases in each sample. However, the XRD pattern for AlFeBe₄, as shown in Figure 2.32, revealed the presence of two further phases, (Fe,Al)Be₅ and FeAl₂Be₅. Metallographic sample preparation and SEM imaging of the samples were performed to ensure single phases were present. The TiBe₁₂ sample showed a single phase and the FeBe₅ sample showed δ-phase dendrites with interdendritic δ-Be eutectic. Figure 2.33 shows an SEM micrograph of the surface of the AlFeBe₄ arc melted sample, it shows the presence of aluminium and iron rich inclusions as well as small dark carbides [48].

To assess the possible corrosion behaviour of the three intermetallic compositions, a plot of the OCP as a function of pH was produced and the OCP plot is shown in Figure 2.34. The data was collected after 48 h in solution in order to reach a steady state.
Figure 2.34 Plot of the OCP for the three studied intermetallic compositions together with beryllium as a function of solution pH [48].

For AlFeBe₄ the OCP was more negative than beryllium over the pH range 2 - 10.5. This suggests that when the two materials are connected, a galvanic couple is formed and electrons will flow from the intermetallic, resulting in the anodic dissolution of the intermetallic. Above pH 11.5, the positions switch, beryllium is more positive and the anodic dissolution of the beryllium matrix is expected. The OCP of the titanium intermetallic was considerably more positive over the neutral and acidic pH range, > 250 mV for pH 2 - 8, reducing to ~60 mV at pH 12.5. The FeBe₅ intermetallic showed an odd behaviour, unlike either of the other two compositions, in near neutral pH the OCP of FeBe₅ was considerably more positive than beryllium ~500 mV, while in acidic solution it was more negative ~150 mV. In alkaline solutions, the intermetallic was slightly more negative ~100 mV at pH 10.5, before rising to more positive ~150 mV at pH 12.5. It was therefore concluded that in acidic solutions the intermetallic would act as an anode and in neutral or alkaline solutions it would act as a cathode. It was expected that the large potential difference would considerably cathodically polarise the surrounding beryllium matrix, resulting in rapid dissolution of the matrix, in near neutral pH [48].

For a standard solution at pH 7.0 the expectation was that beryllium would undergo anodic attack in the vicinity of the TiBe₁₂ and FeBe₅ while the AlFeBe₄ precipitate would be anodically attacked. However, a much smaller driving force for anodic dissolution of the AlFeBe₄ precipitate is expected than for the anodic dissolution of beryllium surrounding the other two intermetallics.

To further investigate the corrosion effects of the AlFeBe₄ precipitates, samples of beryllium were produced with an area ~16x larger than that of the arc melted AlFeBe₄ intermetallics. These samples were electrically connected over the pH range 2 - 12.5. The AlFeBe₄ was found to behave anodically with respect to beryllium over the pH range 2 - 10, and cathodically at pH 12.5. The couple current and potential were measured in each solution and the results are shown in Table 2.14.
Table 2.14 Results from a galvanic corrosion couple between beryllium and AlFeBe₄. A positive current indicates electron flow to the beryllium [48]

<table>
<thead>
<tr>
<th>Solution pH</th>
<th>Cathode : anode area ratio</th>
<th>Couple current (µA)</th>
<th>Couple potential (V vs. MMSE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>16.3</td>
<td>+0.049</td>
<td>-1.00</td>
</tr>
<tr>
<td>7.2</td>
<td>16.3</td>
<td>+0.075</td>
<td>-0.86</td>
</tr>
<tr>
<td>10.5</td>
<td>16.3</td>
<td>+0.008</td>
<td>-1.03</td>
</tr>
<tr>
<td>12.5</td>
<td>15.9</td>
<td>-0.084</td>
<td>-1.07</td>
</tr>
</tbody>
</table>

Further to the investigation of the AlFeBe₄ precipitate, a cast button containing 10 vol% iron and 90 vol% beryllium was fabricated. XRD showed that the FeBe₅ beryllide was present, as well as the host beryllium. The sample was exposed to aerated solutions of pH 2 for 24 hours, pH 7.2 for 21 hours and pH 12.5 for 48 hours. The samples were examined by SEM to look for the effects of galvanic corrosion. Figure 2.35 shows the SEM micrographs collected from the samples following exposure. They showed: (a) the FeBe₅ was dissolved in the pH 2 solution while the beryllium matrix remained intact, as expected from the OCP. (b) In the pH 7.2 solution the FeBe₅ remained unattacked while the surrounding matrix was severely corroded, as expected (c). In the pH 12.5 solution there was little evidence for corrosion although a few pits on the surface showed signs of active beryllium dissolution they displayed a morphology expected for crystallographic corrosion [48].

Figure 2.35 SEM micrographs of the surface of the beryllium - FeBe₅ mixed phase sample exposed to various pH solutions: (a) pH 2, (b) pH 7.2 and (c) pH 12.5 [48].

Further to the previously described electrochemical studies, an investigation into the pitting corrosion of three forms of beryllium containing different concentrations of impurities focused on the types of inclusions at which pitting appeared to be initiated. The three grades: S-65 bar, S-65 billet and P-10 bar were examined using SEM and EDX to characterise the size and composition of the inclusions [23]. The results are shown in Table 2.15.
Following identification of a range of inclusion types a number of regions were analysed in more depth. SEM micrographs and EDX analysis was performed on a number of inclusions before the sample was polarised in deaerated, pH 7, 0.001 M KCl. After which the same regions of the sample surface were imaged and analysed.

Corrosion pits were found to initiate at second phase particles present at the grain boundaries. It was noted that the majority of pits initiated at the AlFeBe$_4$ precipitates, with one at elemental silicon and some at mixed carbide inclusions. For the carbide particles it was found that, as expected, the inclusions themselves dissolved leaving behind an empty pit. For the AlFeBe$_4$ and elemental silicon sites it was found that initiation occurred at the interface between the particles and the matrix, with the apparent dissolution of the matrix, indicating that the AlFeBe$_4$ inclusions were nobler than the surrounding beryllium at pH 7 [23]. This is in contrast to the previous electrochemical investigation that found the AlFeBe$_4$ precipitate should be anodic to the beryllium matrix at pH 7, although that investigation was carried out in the absence of aggressive ions and with a multiphase sample. No evidence for the initiation of corrosion pits at beryllium oxide inclusions was found. It was previously suggested that the heterogeneity between oxide particles and the metal matrix could provide an initiation site for pitting corrosion [34].

### 2.18 Research gap

Reviewing the available literature regarding the corrosion of beryllium reveals where experimental attention should be focused to further develop the understanding of beryllium corrosion. The earliest corrosion studies used traditional methods of counting the number of pits and examining the depth to which the pits penetrated beryllium, in various solutions, over time. Experimental investigations developed further and electrochemical polarisation studies began to form the basis of the research. While these studies have provided a wealth of information regarding the general behaviour of beryllium and the conditions under which it corrodes, the specific role of second phase particles cannot be clearly obtained utilising these methods.

The latest research has moved away from electrochemistry and has begun to examine the effects of discreet second phase particles in beryllium. By moving in this direction it has become possible to identify the most important second phase particles in the corrosion process.
The next logical step would be to investigate the microchemistry of the second phase particles that are believed to have an active role in the corrosion processes of beryllium. This can be achieved through the use of the experimental methodology developed in this thesis, whereby: a range of inclusions of varying composition are selected and their positions on the surface marked. They are then imaged in an SEM and then high spatial resolution surface analysis is combined with a bulk analysis technique to analyse the inclusions. The sample is then repeatedly exposed to a corrosive solution and the previously marked inclusions are reanalysed in the same orientation.

2.19 Use of combined SEM/EDX with AES analysis for the study of pitting corrosion

The surface analysis laboratory at the University of Surrey has a long history in the utilisation of an instrument with combined Auger electron spectroscopy and energy dispersive x-ray spectroscopy. This allows the in-situ acquisition of surface, <10 nm, and bulk, ~1-2 μm, information respectively. Combining the techniques provides a wealth of information about the sample and the initiation of pitting in a material and has helped further develop the understanding of the processes involved in the pitting corrosion of: steels [54,55], aluminium/SiC metal matrix composites [56], and aluminium alloys [57].

The first thorough investigation using these techniques studied the pitting corrosion of 316 stainless steel. The second phase particles of interest were MnS and oxide inclusions. A reliable method allowing the repeated analysis of the same inclusion in the same geometry was developed as part of the study. Vickers microhardness indentations were placed around the inclusions of interest allowing alignment of the SEM FOV with the inclusion. This method of marking the areas of interest has been used in all subsequent investigations. Utilisation of EDX in the investigation identified that oxide particles were not homogeneous but contained nodules of MnS and contained a complex mixture of chromium, titanium aluminium and manganese. Upon exposure to a 3.5 wt.% NaCl solution, at pH 7, for 450 minutes EDX revealed a significant depletion in the signal intensity from the bulk of the particle and an increase in the intensity of a matrix peaks. AES maps of the inclusion showed a drop in the sulphur peak intensity from the inclusion and sulphur was observed to be present on the surrounding surface. The results revealed the active dissolution of the MnS inclusions relative to the surrounding cathodic matrix [54,55].

Another material investigated using this methodology was SiC/6061 aluminium metal-matrix composites. In this investigation the experimental method was further developed. By sequentially exposing the sample to known concentrations of magnesium chloride including: 0.001 M, 0.01 M and 0.1 M it was possible to positively determine the regions of the material that were cathodic and estimate their cathodic current density. The investigation showed that impurities elements present in the alloy formed second phase particles that were responsible for micro galvanic corrosion. AES of the intermetallics before and after exposure to a 3 wt.% NaCl solution revealed the enrichment of oxygen at their location which was believed to be aluminium hydroxide corrosion products. No magnesium deposition was observed on the SiC particles. However, magnesium was observed in AES spectra collected from the surface of intermetallic particles and was not present on the surrounding matrix. This showed the intermetallics to be cathodic with respect to the matrix. It
was also possible to estimate the cathodic current density of the intermetallics as 0.7 mA cm$^{-2}$ by bracketing the critical concentration of magnesium chloride solution required to deposit magnesium hydroxide on the intermetallic surfaces [56].

The most recent studies utilising this technique have examined the role of individual second phase particles in 2219 aluminium alloy. The study tracked three intermetallics over a 16 hour immersion time in 3.5 wt.% NaCl solution. By performing AES and EDX mapping after various immersion times it was shown how the initial corrosion of the intermetallics developed. Copper rich intermetallics were found to act as pitting initiation sites with the gradual deposition of aluminium hydroxide and iron hydroxide corrosion products. An insoluble copper chloride film was also found to initially form on the copper rich intermetallic surface. Additionally, it was revealed that small cathodic intermetallics could be undermined and released from the surface because of the gradual removal of the surrounding matrix [57].

**2.20 Auger electron spectroscopy**

Two previous studies have analysed beryllium using Auger electron spectroscopy [58,59]. Although, neither investigated the corrosion of beryllium, they focused on the oxidation of a clean beryllium surface and the chemical information contained within the Be $KLL$ Auger transition.

High purity, 99.9%, beryllium films were evaporated in UHV onto two substrates. One was polished stainless steel and the other was glass. AES on these films showed a large peak at 104.5 eV identified as the $KLL$ transition of beryllium metal, with two small peaks at 84 eV and 60 eV believed to be plasmon losses of the main beryllium peak.

The AES spectra collected during the gradual oxidation of beryllium, from one of the investigations are shown in Figure 2.36. The investigation showed the peaks responsible for the $KLL$ Auger transitions for beryllium and beryllium oxide. On clean metallic beryllium, the $KLL$ transition was recorded at 104.5 eV. As the surface was oxidised, the $KLL$ for the oxide began to appear at 94 eV. When the surface was fully oxidised the $KLL$ transition for metallic beryllium disappeared and the remaining peak at 94 eV was the primary Auger transition for beryllium oxide.
2.21 Conclusions

In this chapter the details regarding the corrosion of beryllium have been described and highlighted from the available literature. Reviewing the literature has shown that the chloride ion concentration is more important than the pH of the corrosive media as a logarithmic relationship between the pitting potential and chloride concentration was found whilst a linear relationship has been observed for pH. The review has also shown that the most widely encountered and important aggressive ion is chloride. The presence of chloride ions as well as other ions has been shown to initiate pitting corrosion but chloride is the most widely studied and understood.

The importance of second phase particles in the corrosion process was emphasised, as these represent potential initiation sites for pitting corrosion. The most important particles were found to be the AlFeBe₄ precipitate, iron beryllides and carbide inclusions.

A useful analytical approach to study corrosion of beryllium, paying particular attention to the role of the second phase particles, is the use of combined AES, EDX and SEM. Previous studies employing these techniques for aluminium alloys and stainless steels samples have been briefly described in the last section of this chapter. In the next chapter these analytical techniques will be described, in addition to x-ray electron spectroscopy (XPS) and wavelength dispersive x-ray spectroscopy (WDX) which was also used in this work.

Figure 2.36 AES spectra collected during gradual oxidation of a high purity beryllium foil: (a) metallic beryllium. (b) partially oxidised beryllium and (c) fully oxidised beryllium [59].
Chapter 3 - Experimental Analysis Techniques

3.1 Introduction

In this Chapter the experimental analysis techniques used in this work and their related theory are described. The purpose of the experimental work presented herein was to monitor and investigate the corrosion processes associated with second phase particles in aluminium 7075-T6 and S-65 beryllium as a function of time.

These second phase particles or intermetallics are present in the metals with a range of sizes, typically 0.5-30 µm. Corrosive processes are expected to occur at sites which lack homogeneity such as the matrix-particle interface or grain boundaries. Aluminium and beryllium are known to be covered in a passivating oxide film ~3 nm in thickness. Corrosion initiates in the first few atomic layers of the surface which is exposed to corrosive media. It is expected that initiation is most likely at the matrix-particle interface where a discontinuity in the oxide exists. Here it is expected that corrosion occurs with the gradual dissolution of the host matrix or the second phase particle, resulting in the breakdown of passivity.

Analysis of second phase particles requires a technique with a lateral resolution significantly better than the size of the second phase particles, to be able to resolve the entire interface of the particles. An important consideration in the investigation of corrosion is the depth of analysis. This is because corrosion initiation occurs at the extreme surface, probing too far into the bulk material causes a loss of information about this surface process. These requirements are met through the use of Auger electron spectroscopy (AES). This technique provides a lateral resolution of <15 nm and a depth of analysis <10 nm.

By pairing AES with in-situ energy dispersive x-ray spectroscopy (EDX), information about the bulk and surface of the region of interest can be collected simultaneously. Another technique of great use for the investigation of corrosion is X-ray photoelectron spectroscopy (XPS). This technique lacks the spatial resolution of AES, achieving spot sizes of ~15 µm at best, it is just as depth sensitive as AES and is able to resolve the chemical state of the surface atoms and perform quantification.

Throughout this Chapter spectra are presented to illustrate points relevant to the text, unless these are specifically referenced, they represent original data collected as part of the research work.

3.2 Auger electron spectroscopy (AES)

3.2.1 The Auger process

AES is a surface analysis technique based upon the emission of Auger electrons and is named after Pierre Auger (1923) but the emission process was first observed by Lise Meitner in 1922 [60]. The process by which Auger electrons are generated involves three electrons undergoing ionisation, relaxation and emission, from the electron orbitals of an atom.
The energy of the emitted Auger electron can be calculated as being approximately equal to the energy required (ionisation energy) to remove the core electron minus the energies required to remove the additional two electrons involved from their original energy levels, as shown in Equation 3.1 for the $KL_2,L_3$ Auger electron [61]:

$$E_{KL_2,L_2,L_3} \approx E_K - E_{L_2,L_3} - E_{L_2,L_3} \quad (3.1)$$

Where:

$E_K$ is the $K$ shell binding energy and $E_{L_2,L_3}$ is the $L_{2,3}$ shell binding energy.

Figure 3.1(a) shows the effect of an incident electron (AES) or incident photon (X-AES) on a fluorine atom. Providing that the kinetic energy of the incident radiation is great enough, the $K$ electron will be ejected creating a core hole (as denoted by an empty circle). Figure 3.1 (b) Shows the relaxation of the excited atom whereby the core hole is filled by an electron from the $L_{2,3}$ shell. The internal transition leaves an electron hole in the $L_{2,3}$ shell and the energy released by this relaxation is equal to the energy difference of the two shells involved ($E_K - E_{L_{2,3}}$). Figure 3.1 (c) Shows the emission of the $KL_2,L_2,L_3$ Auger electron. The emission energy is provided by the relaxation of the $L_{2,3}$ electron to the core hole, Auger emission leaves the doubly ionised final state (as denoted by the two empty circles).

An example, using copper, to illustrate why Equation 3.1 is only used an approximation of energy values is shown below for the Cu $L_3M_{4,5}M_{4,5}$ Auger transition:

$$Cu\ L_3 M_{4,5} M_{4,5} = L_3 - M_{4,5} - M_{4,5}$$

$$Cu\ L_3 M_{4,5} M_{4,5} = 932.7 \text{ eV} - 1.6 \text{ eV} - 1.6 \text{ eV}$$

$$Cu\ L_3 M_{4,5} M_{4,5} = 929.5 \text{ eV}$$

Given that the primary copper metal Auger transition $L_3M_{4,5}M_{4,5}$ is observed at 918 eV, a more robust method for the Auger electron energy calculation is required. In this case, it is possible to adjust the equation to take into account that while the first two electrons $L_3$ and $M_{4,5}$ are removed and rearranged in atom of
atomic number $Z = 26$ the final electron, $M_{4,5}^*$, is ejected from an atom with a missing electron, this decreases the screening of the nucleus by the electron cloud. Resulting in the Auger electron being ejected from an atom with an effective atomic number of $Z = 27$. The adjusted equation is shown in Equation 3.2 [61]:

$$E_{KL_{2,3}} \approx E_K (Z) - [E_{L_{2,3}} (Z) + E_{L_{2,3}} (Z+1)]$$  \hspace{1cm} (3.2)

Another example using Equation 3.2 is shown for the same Cu $L_3M_{4,5}M_{4,5}$ Auger transition but this time accounting for the change in effective atomic number.

$$Cu \ L_3M_{4,5}M_{4,5}^* = L_3 - M_{4,5} - (Z + 1)M_{4,5}$$

$$Cu \ L_3M_{4,5}M_{4,5} = 932.7 \text{ eV} - 1.6 \text{ eV} - 10.2 \text{ eV}$$

$$Cu \ L_3M_{4,5}M_{4,5}^* = 920.9 \text{ eV}$$

By increasing the atomic number of the atom from which the final electron is emitted a more accurate kinetic energy of the Auger electron is obtained. In this example the final $M_{4,5}$ electron has been calculated as being emitted from a zinc electron orbital, with a kinetic energy 8.6 eV greater than that of the copper orbital.

Moving through the periodic table to higher mass elements, increases the number of occupied electron orbitals that can become involved with the Auger process. This results in a wider range of transitions observed for higher mass elements, within a typical, $0-2200 \text{ eV}$, AES spectrum. For example, beryllium ($Z = 4$) is only capable of the $KLL$ ($100 \text{ eV}$) series of transitions, while copper ($Z = 26$) is capable of the $LMM$ ($750-900 \text{ eV}$) and $MNN$ ($50 \text{ eV}$) series of transitions.

Two competing relaxation processes occur after an atom has been excited by the primary electron beam. These are Auger electron emission and x-ray generation. Figure 3.2 shows the probability of these two relaxation processes occurring as a function of increasing atomic number for a K shell ionisation. The Auger transition is the dominant process up the last element of the 3d transition metal series, e.g. germanium [61].

![Figure 3.2 Probability curves for Auger and x-ray emission as a function of atomic number [61].](image-url)
3.2.2 Depth of Analysis

3.2.2.1 Theory

The depth of analysis in Auger and photoelectron spectroscopy varies with the kinetic energy of the emitted electrons. Auger and photoelectrons are generated within the entire interaction volume of the primary electron beam and x-ray envelope for each technique respectively, the distance from which those electrons are able to escape the surface, without undergoing inelastic collisions, is known as the attenuation length (\( \lambda \)). It is usually taken as being interchangeable with the inelastic mean free path (IMFP) although this is \( \sim 10\%-20\% \) greater than the attenuation length [62]. The attenuation length is the experimentally derived value while the IMFP is derived from theory.

A number of approaches have been investigated in order to connect the attenuation length to the electron kinetic energy and a material property. The most commonly accepted formula for inorganic materials is shown in Equation 3.2 [63]. The equation is slightly different for elements, inorganic materials, and organics.

\[
\lambda = \frac{538\alpha}{E^2_A} + 0.41\alpha_A(E_A)^{0.5} \quad (3.2)
\]

Where:

- \( E_A \) is the kinetic energy of the electron in eV,
- \( \alpha \) is the atomic radii in nm and
- \( \lambda \) is the attenuation length in nm.

Figure 3.3 shows the change in signal intensity as a function of electron escape depth. It considers electrons that emerge at 90° to the sample surface (emission angle of 0°), 65% of the signal escapes from a depth <\( \lambda \), 85% escapes from <2\( \lambda \) and 95% escapes from <3\( \lambda \). The attenuation length is not usually more than 3.5 nm, therefore the depth of analysis is limited to <10 nm for typical laboratory AES and XPS instruments [64]. The difference in signal intensity as a function of emission angle is exploited in angle resolved XPS and AES.

![Figure 3.3](image_url)  
Figure 3.3 Schematic of the intensity as a function of the depth of analysis. The dashed line indicates a depth of \( \lambda \) [64].
The depth of analysis is a function of the analysed electrons kinetic energy, as such it is possible to observe the different depths of analysis within a single spectrum. Figure 3.4 shows this effect for the Mg 1s, 2s and 2p photoelectron peaks collected from a magnesium surface and analysed using a monochromatic aluminium x-ray source. These were acquired as part of the work in Chapter 8. The spectra illustrate the changing depth of analysis moving through the spectrum. The reported depths of analysis are taken as $3\lambda \cos(\theta)$ in each case.

(a) Shows the Mg 2p transition with a binding energy of 50 eV, kinetic energy of 1430 eV and a depth of analysis of $\sim 6.9$ nm. This transition has the highest kinetic energy of the three and so the metal peak is the most intense. (b) Shows the Mg 2s transition with a binding energy of 90 eV, kinetic energy of 1400 eV and a depth of analysis of $\sim 6.7$ nm. (c) Shows the Mg 1s transition with a binding energy of 1305 eV, kinetic energy of 180 eV and a depth of analysis of $\sim 1.6$ nm. The Mg 1s transition has the lowest depth of analysis as it is the lowest kinetic energy. At this kinetic energy the majority of the electrons from the metal are attenuated within the surface oxide and so the oxide peak is considerably more intense than the metal peak.

The depths of analysis were calculated using IMFP and $3\lambda \cos\theta$. The thickness of the oxide was calculated as 2.5 nm.

![Figure 3.4 High resolution Mg 2p (a), 2s (b) and 1s (c) spectra collected from a pure magnesium sample with an air formed oxide.](image)

### 3.2.2.1 Angle resolved AES and XPS

The intensity of electrons, $I$, emitted at an angle $\theta$ to the surface normal is given by the Beer-Lambert equation 3.4 [64]:

$$I = I_0 \exp \left(\frac{-d}{\lambda \cos \theta}\right) \quad (3.4)$$

Where:

- $I$ is the measured peak intensity, $I_0$ is the intensity from an infinitely thick sample, $d$ is the depth of electron emission, $\lambda$ is the attenuation length of the emitted electron and $\theta$ is the electron take off angle relative to the sample normal.

The equation can be rearranged to show how the depth of analysis varies as a function of the emission angle $\theta$, as shown by Equation 3.5:

$$d = -\lambda \cos \theta \ln \left(\frac{I}{I_0}\right) \quad (3.5)$$

This is exploited to enable the acquisition of non-destructive depth profiles in both conventional and parallel angle resolved XPS. Figure 3.5 shows how the depth of analysis changes as a function of the emission angle.
For emission normal to the sample surface ($\theta = 0$), the greatest depth of analysis is achieved. This is $\sim 3\lambda$ and results in a maximum depth of analysis of $\sim 10$ nm. At near grazing angle emission ($\theta = 75^\circ$) the depth of analysis is $\sim 0.8\lambda$ resulting in signal from $\sim 2.4$ nm.

![Diagram showing sampling depth as a function of electron "take off" angle or "emission" angle ($\theta$), relative to the sample normal in electron spectroscopy.]

Conventional angle resolved AES or XPS involves tilting the sample to change the emission angle. This can present a number of problems for the user. Firstly, only small samples can be tilted within the instrument without colliding with the various internal components. Secondly, the sample stage must be carefully controlled during tilting to ensure that the original area of interest remains in the correct position, because tilting changes the focal point on the sample if the region of interest is not centred. Thirdly, upon sample tilting the spot size changes as a function of the $\cos(\theta)$ whereby a tilt of $60^\circ$ in conventional angle resolved XPS will elongate a 400 μm analysis spot to 800 μm.

An example of conventional angle resolved AES performed in the MICROLAB 350 at Surrey is shown in Figure 3.6. In (a) the sample has been tilted $15^\circ$ away from the analyser to achieve grazing emission ($\theta = 75^\circ$) and a depth of analysis of $\sim 2.4$ nm, for Al $KLL$. In (b) the sample has been tilted $60^\circ$ towards the analyser to achieve normal emission ($\theta = 0^\circ$) and a depth of analysis of $\sim 9.3$ nm for Al $KLL$. The increase in analysis depth is apparent from the change in the metal and oxide peak intensities. In (a) the Al $KLL$ oxide peak centred at 1386 eV is more intense than the Al $KLL$ metal peak at 1393 eV as the majority of the signal escapes from the surface oxide. In (b) the reverse is true as a much greater proportion of the generated Auger electrons escape from the metal underneath the oxide. For an electron of kinetic energy 1400 eV, generated in aluminium, the IMFP was calculated as $\sim 3.1$ nm. The depths of analysis were calculated using $3\lambda\cos(\theta)$ [64].
Chapter 3

Analysis Techniques

Figure 3.6 High resolution Al KLL spectra to highlight the change in analysis depth upon changing from grazing to normal electron emission by tilting the sample in AES: (a) grazing emission $\theta = 75^\circ$ and (b) normal emission $\theta = 0^\circ$.

Within the Thermo Scientific MICROLAB 350 Auger microscope it is not possible to perform parallel angle resolved spectroscopy as the electron detector after the hemispherical sector analyser (HSA) is not equipped for it. The HSA in the Thermo Scientific Theta Probe does not possess the innate problems associated with conventional angle resolved x-ray photoelectron spectroscopy (ARXPS). The detector in the Theta Probe consists of a two dimensional array of channeltrons in a channelplate while the MICROLAB detector consists of six individual channeltrons. This enables the Theta Probe detector to preserve the angular information of the electrons from the surface emitted. Channeltrons can be dedicated to acquire one particular angle of emitted electrons. The sample does not need to be tilted to acquire the angle resolved data and so large samples can be analysed, the point of interest remains in focus and there is no x-ray spot elongation.

An example of parallel angle XPS is shown in Figure 3.7. The spectra highlight how the ability to choose between grazing angles or near normal emission angles in the Theta Probe can be advantageous to the user. Here ARXPS was utilised to look for sulphur contamination at the extreme surface. The sulphur was believed to be contributing to the failure of a metal diffusion bond. For an electron of kinetic energy $1320$ eV, S 2p, the IMFP is calculated as being $2.9$ nm [63]. Figure 3.7 (a) shows the spectrum produced from the electrons collected with grazing emission, $\theta = 70^\circ$ and a depth of analysis of ~3 nm. It illustrates the enrichment of sulphur containing material at the surface of the sample. (b) Shows the spectrum produced from the electrons collected with near normal emission, $\theta = 10^\circ$ and a depth of analysis of ~8.6 nm. A significant drop in peak intensity is observed indicating that sulphur is concentrated at the surface.
3.2.3 Instrumentation

3.2.3.1 Auger microscope

The spectrometer used for Auger electron spectroscopy was a Thermo Scientific MICROLAB 350, equipped with a Schottky field emission electron gun, secondary and backscattered electron detectors, an energy dispersive x-ray detector, twin anode x-ray source and a hemispherical sector analyser. Figure 3.8 and Figure 3.9 show the front and side views of the Auger microscope. They show how it is possible to perform a range of analysis techniques on the sample without removing it from the vacuum. The procedure for analysis is: a sample is loaded into the fast entry lock (13) and it is usually left for twenty minutes to be evacuated to $1 \times 10^{-7}$ mbar by a turbo molecular pump, after which a gate valve is opened and the sample is transferred to the preparation chamber (12). This chamber is evacuated to $1 \times 10^{-9}$ mbar using the ion pump (14). From here, the sample is moved using a high precision mechanical assembly into the analysis chamber (9). The analysis chamber pressure is typically $1 \times 10^{-7} - 1 \times 10^{-10}$ mbar. The UHV is achieved through the combination of an ion pump and a titanium sublimation pump. Once the sample is in the analysis position in the analysis chamber it is secured using a mechanical lock to ensure it does not shift when the stage is repositioned. The sample stage can be moved in the x, y and z directions by approximately 20 mm, tilted from -20° to +90°, or rotated 360° from the initial position by the five stage motors (3) operated by the stage controller (4).
Figure 3.8 Picture of the Thermo Scientific MICROLAB 350 microscope. Components of note are highlighted: (1) EDX detector, (2) gun apertures, (3) stage motors, (4) stage controller, (5) objective aperture, (6) backscattered detector (not included in this image), (7) electron gun, (8) hemispherical analyser, (9) analysis chamber, (10) secondary electron detector, (11) fracture stage, (12) preparation chamber, (13) fast entry lock and (14) preparation chamber ion pump.

Figure 3.9 Picture of the side view of the Thermo Scientific MICROLAB 350 microscope, (15) electron gun ion pump, (16) EX05 argon ion gun and (17) twin anode Al/Mg x-ray source.

From the sample starting position the sample can be analysed by AES (7) and by EDX (1). The sample can also be imaged using the secondary electron (10) or backscattered electron detectors (6). The gun (2) and objective (5) apertures can be adjusted to change the sample current for improved specimen imaging or increased Auger intensity. The EX05 argon ion gun (16) can be used lightly sputter the sample surface to remove contamination, perform an AES depth profile or to flood the sample with low energy argon to act as charge compensation, allowing the analysis of insulating samples. The twin anode XPS source (17) is placed at 60° below the analyser requiring the sample to be moved from the normal “home” position.

3.2.3.2 Instrument geometry

The electron column is perpendicular to the sample surface when the sample is in the “home” starting position. The transfer lenses are placed at 60° from the electron column, resulting in an electron emission
angle of 60° from the sample normal. The transfer lens has a cone angle of 25° resulting in electron collection from emission angles of 85° to 35°, to the analyser. To the side of the electron analyser is the EDX detector mounted at 55°. Opposite this is the SE detector also mounted at 55° and next to this is the EX05 ion gun mounted at 67.5°. Some of these are shown in Figure 3.10.

As shown in Figure 3.11 the twin anode XPS source is placed at 60° below the analyser. When the sample is not tilted XPS analysis cannot be performed. After tilting 30° the surface starts to be exposed to the twin anode. The maximum tilt angle is 60°, which results in normal electron emission. The red arrow represents the primary electron beam.

An example of the effect of the ion gun geometry on the sample surface is shown in Figure 3.12. (a) Shows the position in which the ion gun is mounted with respect to the sample surface in the microscope. (b) Shows the effect of performing argon ion sputtering on a beryllium surface when small contamination particles are present. The surface behind the particles is shielded from the argon ions during bombardment and so these regions appear lighter in the SEM image. This is because the native oxide is still present in these regions which have a higher electron yield than the surrounding oxide-free beryllium metal surface. If etching if continued without the use of Zalar rotation the shadowing effect can become highly pronounced, with the formation of surface nodules pointing in the direction of the ion gun [67].
3.2.3.3 Electron source

The purpose of the electron source in AES is to produce a finely focused primary electron beam that can eject electrons from the core energy levels of surface atoms. The process is most efficient when the primary electron energy is greater than 3-5x the ionisation energy of the core level. The scanned energy range in AES is usually 0-2200 eV as all elements have Auger transitions in this energy range. Therefore, a primary beam energy of 10-15 keV is more than sufficient to maximise the excitation cross section.

A number of different electron sources are used in Auger spectrometers and microscopes, these are usually grouped as thermionic or field emission sources. Examples of each type are shown in Figure 3.13. The thermionic sources consist of either a tungsten wire fabricated into a hairpin (a) or a lanthanum hexaboride single crystal shaped as a fine cone (b). These are heated to 2300 K or 1800 K respectively to allow electrons to overcome the material work function and be ejected from the apex of the source. The ejected electrons are then focused onto the sample surface through the electron column. Thermionic emitters are inexpensive and robust. They do not require the top end UHV of field emission sources. However, they lack brightness and so tend not to have spot sizes smaller than 100-200 nm.

Field emission sources can be divided into cold and hot (thermally emitted) types. The cold field emitter consists of a small piece of single crystal tungsten attached to a tungsten wire hairpin (c). The tip of the single crystal forms a cone with a radius of 20-50 nm. The tip is placed inside a large electrostatic field to allow quantum tunnelling of the electrons from the tip. Therefore, the electrons do not need to overcome the
work function of the metal and so the source does not need to be heated. While cold FEG sources are able to provide much greater spatial resolution compared to thermionic sources they suffer from poor long term stability. As a consequence of their low operating temperature, gases absorb onto the tip, contaminating it and affecting the emission current.

The most popular choice of electron source is that fitted in the MICROLAB 350. This is a hot field emitter or a Schottky field emitter (d). It is a combination of the thermionic and field emission source types. It is similar to the cold field emitter in that it consists of a small piece of single crystal tungsten attached to a tungsten wire formed into a hairpin. The tungsten crystal is formed into a cone and it is coated with zirconium dioxide. The role of the ZrO₂ semiconductor is to lower the work function, increase the emission current and to provide a self-cleaning and self-healing surface [64].

The source consists of a tungsten tip with a radius of 20-50 nm which is heated to 1800 K and placed inside a large electrostatic field, the combination of the heat and the field causes electrons to be emitted. As the tip is operated at high temperatures, it avoids the contamination problems associated with the cold FEG source. Table 3.1 shows a comparison of all four electron emitters.

In a high performance Auger microscope a Schottky FEG is almost universally used while in a multi technique XPS instrument a LaB₆ emitter will usually suffice. The Schottky field emitter gives a better signal intensity, lateral resolution and has far superior brightness to the thermionic source. With 1 nA of sample current and 10 keV beam energy the Schottky field source produces a 10 nm spot size, compared to the 100 nm spot of the LaB₆ source under the same conditions [64].

Table 3.1 Comparison of electron source properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Tungsten filament</th>
<th>LaB₆</th>
<th>Cold FEG</th>
<th>Schottky FEG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Work function (eV)</td>
<td>4.5</td>
<td>2.7</td>
<td>4.5</td>
<td>2.95</td>
</tr>
<tr>
<td>Brightness (Acm⁻² srad⁻¹)</td>
<td>&lt;10⁵</td>
<td>−10⁹</td>
<td>10⁷ to 10⁹</td>
<td>&gt;10⁸</td>
</tr>
<tr>
<td>Max beam current (nA)</td>
<td>1000</td>
<td>1000</td>
<td>20</td>
<td>200</td>
</tr>
<tr>
<td>Operating temperature (K)</td>
<td>2300</td>
<td>1800</td>
<td>300</td>
<td>1800</td>
</tr>
<tr>
<td>Long term stability</td>
<td>High</td>
<td>High</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Vacuum required (mbar)</td>
<td>&lt;10⁻⁴</td>
<td>&lt;10⁶</td>
<td>&lt;10⁻¹⁰</td>
<td>&lt;10⁻⁸</td>
</tr>
<tr>
<td>Typical lifetime (h)</td>
<td>&lt;200</td>
<td>~1000</td>
<td>&gt;2000</td>
<td>&gt;2000</td>
</tr>
<tr>
<td>Relative cost</td>
<td>Low</td>
<td>Medium</td>
<td>High</td>
<td>High</td>
</tr>
</tbody>
</table>

3.2.3.4 Electron column

The role of the electron column is to focus the electrons that are emitted from the Schottky field emission gun, into a small spot on the sample surface. The column of the MICROLAB 350 has two magnetic lenses, a condenser (gun) lens just below the source, alignment coils and an objective lens at the bottom of the column. The magnetic lenses are used for focusing in preference to electrostatic lenses because they have a smaller aberration coefficient, resulting in a sharper, brighter, spot at the sample surface. The objective lens is used to improve the imaging contrast by blocking the stray electrons from the edge of the beam. It is usually left out for AES and SAM. The alignment coils are adjusted to shift (x-y position) and tilt (angle) of the electron beam. Four stigmator coils are also present and are adjusted to reduce astigmatism.
The most important aspects of the column for typical users are the gun apertures. They allow convenient adjustment of the spatial resolution and sample current without modifying the gun settings. There are four gun apertures to choose from, with diameters of 50, 70, 100, 150 µm. The aperture can also be completely removed. The results of changing the aperture and beam energy on spatial resolution and sample current are shown in Table 3.2. These were measured using a gold nano island on carbon sample, without the objective aperture and with the turbo molecular pumps and stage control off to reduce noise. The gold island sample consists of many thousands of small (< 1 nm - 100 nm) gold droplets on a carbon substrate. The large difference in atomic mass between gold and carbon provides an excellent contrast difference in secondary electron imaging. This allows a profile to be drawn across the interface between a gold island and the carbon substrate, in the SEM image, to measure the distance the minimum and maximum signal intensity. This distance is taken as the spatial resolution of the microscope.

By using the smallest aperture size the sample current can be reduced to < 1 nA, producing a spot size of 11 nm with a 10 kV beam. The highest achievable spatial resolution was 6 nm with a 25 kV beam (not shown in table). However, this required significant analysis time and preparation and so 11 nm represents a better value of the spatial resolution with aperture 1 (50 µm) under normal operating conditions. While the spatial resolution is highest under these conditions, the reduction in sample current significantly decreases the intensity of Auger spectra and so aperture 1 is only used for high resolution SEM work. Aperture 3 (100 µm) was deemed to be a good compromise between Auger intensity and resolution for SAM mapping in this project. The AES spatial resolution including the backscattered effect was about 40 nm.

Table 3.2 SEM spatial resolution and sample current at varying beam energies and gun aperture sizes for the MICROLAB 350

<table>
<thead>
<tr>
<th>Aperture</th>
<th>Beam energy (keV)</th>
<th>Sample current (nA)</th>
<th>SEM resolution (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aperture 1 (50 µm) - high resolution SEM imaging</td>
<td>10</td>
<td>0.70</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0.71</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.85</td>
<td>10</td>
</tr>
<tr>
<td>Aperture 2 (70 µm) high resolution SEM imaging and low current AES</td>
<td>10</td>
<td>1.5</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>1.4</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1.7</td>
<td>11</td>
</tr>
<tr>
<td>Aperture 3 (100 µm) - routine Auger analysis</td>
<td>10</td>
<td>2.8</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>3.1</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>3.4</td>
<td>13</td>
</tr>
<tr>
<td>Aperture 4 (150 µm) - high sensitivity Auger analysis</td>
<td>10</td>
<td>6.5</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>6.8</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>7.3</td>
<td>25</td>
</tr>
<tr>
<td>No aperture - Fast, high sensitivity Auger analysis</td>
<td>10</td>
<td>41.0</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>46.8</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>47.3</td>
<td>20</td>
</tr>
</tbody>
</table>
3.2.3.5 Analyser

The analyser is used to measure the kinetic energy of the electrons emitted from the sample in order to obtain a spectrum. There are two types of electron energy analyser used in AES: the cylindrical mirror analyser (CMA) and the hemispherical sector analyser. Each has its own advantages and disadvantages. The MICROLAB 350 is fitted with a HSA. It consists of two hemispherical electrodes with a central gap through which electrons can travel, as shown in Figure 3.14.

![Schematic of a hemispherical sector analyser](image)

Figure 3.14 Schematic of a hemispherical sector analyser [61].

A potential difference is applied across the two hemispheres with $V_2$ greater than $V_1$. Electrons entering the analyser will only reach the detector if their energy is given by Equation 3.6:

$$E = e\Delta v \left( \frac{R_1 R_2}{R_2^2 - R_1^2} \right)$$  \hspace{1cm} (3.6)

Where:

- $E$ is the kinetic energy of the electron in eV,
- $e$ is the electron charge in eV,
- $\Delta v$ is the potential difference applied between the two hemispheres $V_1$ and $V_2$ and $R_1$ and $R_2$ are the radii of the inner and outer hemispheres respectively.

From this equation an electron entering into the analyser with the correct kinetic energy $E = eV_0$ will travel through the analyser along the median equipotential surface of radius $R_0$, and it will be focused onto the detector at the exit. Electrons that enter the analyser with more or less energy than $E$ will deviate from the median equipotential radius through the detector and so will not be focused at the detector. Electrons for which the deviation in $E$ is low, will follow $R_0$ closely and result in a degree of energy spread at the detector. By placing numerous detectors at the exit slit $F$, that each collect electrons of a different energy it is possible to increase the sensitivity of the instrument over an equivalent instrument using only 1 detector. Instruments with up to 112 electron channels are now available, each of which can collect a small energy window. This is exploited in XPS and AES instruments to record spectra without scanning the entire energy range of interest.
The analyser can be operated in two modes: constant analyser energy (CAE) also known as fixed analyser transmission (FAT) and constant retard ratio (CRR) also known as fixed retard ratio (FRR). In CAE mode the electrons are retarded or accelerated to a defined energy. This is known as the pass energy, as only electrons of this kinetic energy can travel through the analyser at radius \( R_0 \). Analysis in CAE mode is performed by keeping the voltages of the inner (\( V_1 \)) and outer (\( V_2 \)) hemispheres at a constant potential e.g. the pass energy, as shown in Figure 3.15.

Prior to the entrance of the electron analyser electrons must travel through a metal mesh. This mesh is known as the retarding grid. This grid is held at a potential known as the pass energy. If electrons have a lower energy than the pass energy they cannot traverse the grid. The function of the grid is to reduce the kinetic energy of the electrons entering the analyser so that their trajectory can be more easily controlled. If electrons with a kinetic energy of 1300 eV were to analysed without the retarding grid an analyser with a very large diameter would be needed. Much greater than the typical 0.5 m diameter laboratory analysers.

Selection of a suitable pass energy is important as it affects the signal intensity (transmission) and the energy resolution. Using a low pass energy will provide a high energy resolution but low signal intensity, while a high pass energy will provide a low energy resolution but high signal intensity. This is highlighted in Table 3.3 for the Ag 3d\(_{5/2}\) peak. This peak has the smallest natural line width of any of the photoelectron transitions and so provides a robust measure of the minimum experimental resolution.

<table>
<thead>
<tr>
<th>Pass energy (eV)</th>
<th>Energy resolution (eV)</th>
<th>Relative signal intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.50</td>
<td>1</td>
</tr>
<tr>
<td>50</td>
<td>0.65</td>
<td>55</td>
</tr>
<tr>
<td>250</td>
<td>1.82</td>
<td>450</td>
</tr>
</tbody>
</table>

The pass energy remains constant for all electron kinetic energies as such the resolution also remains the same for all detected electrons. For this reason, CAE mode is used in XPS analysis. In a typical XPS experiment, high pass energies, such as 250 eV, are used for survey spectra so as to identify all elements present in the sample. Low pass energies, such as 20 eV, are used for high resolution spectra in order to identify chemical states and to perform quantification.
In CRR mode, the electrons are retarded by a defined fraction of their original kinetic energy. For example, if the retard ratio is 10, and electrons of kinetic energy 1000 eV are to be detected, then the electrons will be retarded to 100 eV and the pass energy is set to 100 eV. If electrons of energy 1500 eV are to be detected, then the electrons will be retarded to 150 eV and the pass energy is set to 150 eV. To achieve this, the voltages of the inner and outer hemispheres are scanned as shown in Figure 3.16. In CRR mode, the relative resolution (where ΔE is the peak FWHM) is constant for all energies of the electrons. While the absolute resolution (ΔE/E₀), where E₀ is the electron kinetic energy, decreases with increasing kinetic energy. This provides constant resolving power. For this reason CRR is used in AES. The equivalent CAE pass energy in CRR mode can be found by dividing the kinetic energy of the peak of interest by the retard ratio used to collect it. The resolution in CRR mode is approximately equal to two divided by the retard ratio.

HSAs have a much greater energy resolution, compared to CMAs. However, they suffer from lower signal intensity. While a high energy resolution is not a requirement in typical AES analysis, as a consequence of the intrinsic width of Auger transitions, high spectral resolution is important in the analysis of samples from which chemical state information is required. A HSA is capable of achieving resolutions of <0.05%, while a CMA provides an energy resolution of only ~0.5%. The effect of these energy resolutions is shown in Figure 3.17. This shows how much clearer the difference between the aluminium metal and the aluminium oxide peaks are when moving from the resolutions achievable with a CMA to those achievable with a HSA. The metal signal is observed at 1394 eV and the oxide at 1388 eV, a plasmon loss peak is also observed at 1378 eV. It should be noted that the spectra have been normalised and the signal intensity from the spectrum acquired with a resolution of 0.05% was approximately 20x lower than that acquired with a resolution of 0.5%. This can be seen by the decrease in signal to noise as the resolution increases, highlighting the trade-off between signal intensity and resolution.
A problem that arises when using a HSA that does not appear when using a CMA is apparent when dealing with samples that contain significant topography. As the electron gun in a CMA forms part of the analyser the CMA is positioned directly above the sample along the sample normal resulting in an electron emission angle of 0° to the analyser. For a HSA, the electron gun is still mounted along the sample normal but the analyser is mounted at an angle between the sample normal and the sample plane, usually resulting in an emission angle of ~60°. This geometry can cause shadowing within an SAM map, as Auger electrons emitted from areas of the surface located behind high surface features cannot reach the analyser as they are attenuated by the material in front of them, as shown in Figure 3.18. Additionally, areas of intense signal generated from angled features facing the analyser. The same effect is observed in secondary electron imaging, as edges appear bright because of the increased secondary electron yield.

Figure 3.17 AES spectra of an aluminium surface collected with increasing spectral resolution.

These effects are highlighted in Figure 3.19. This shows an SEM micrograph of a copper particle on an aluminium substrate together with Al KLL and Cu LMM maps collected from the SEM FOV using the MICROLAB 350. The blue arrow in the SEM micrograph (a) shows the axis of the secondary electron detector. The side of the particle facing the detector appears bright while the region behind the particle appears shadowed because of the reduced number of electrons reaching the detector. The green arrow in the Al KLL map (b) shows the direction of the transfer lens of the hemispherical analyser. The region of low signal intensity underneath and behind the particle is highlighted by the red arrow in the map (b). The electrons from this region are attenuated by the particle and so do not reach the detector. A region of intense
signal is observed in the copper map (c), highlighted by the red arrow. This is the area of the particle that faces the detector resulting in an increased Auger electron yield.

Figure 3.19 SEM micrograph of (a) a copper particle on an aluminium surface, (b) an Al KLL map and (c) a Cu LMM map collected from the same region.

3.2.3.6 Detector

The purpose of a detector is to count the electrons emitted by the sample after they have been energy filtered by the analyser. There are two types of electron detectors: channel electron multipliers also known as channeltrons, and channel plates.

The first type is used in the MICROLAB 350, which has six channeltrons. A channeltron is a spiral-shaped glass tube with a cone shaped collector at one end and a metal anode at the other. The two ends are kept at high a potential difference. The negative potential is placed on the cone, to accelerate electrons into the tube. The internal walls of the tube are coated with a scintillator material which, when it is hit by an electron of sufficient energy, will excite further electrons. These in turn are accelerated by the potential difference in the walls, colliding with them to generate a cascade of secondary electrons. The amplification of the channeltron results in $\sim 10^8$ electrons exiting the channeltron for each electron that entered and the signal becomes large enough to detect at a pulse amplifier, where the electron can then be counted by the rate meter.

The detector in the MICROLAB 350 consists of six channeltrons, arranged in the dispersive direction of the analyser in order to collect electrons with different kinetic energies. During this project the second channeltron was not functioning. However, this did not have a particularly adverse effect on the instrument performance and so it was not deemed necessary to replace because of the high cost involved.

The second type of detector is utilised in the Theta Probe. This detector has a channel plate consisting of 112 detectors in two dimensional array. Each hole acts as a small channeltron, amplifying the electron count at that point. The grid arrangement enables the acquisition of photoelectron images as well as parallel angle resolved XPS.

3.2.3.7 Transfer lenses

A set of transfer lenses are fitted between the sample and the analyser, as shown in Figure 3.20, these have a number of uses: They allow the analyser to be mounted far enough away from the main chamber to allow access to the sample from other components including the dual anode x-ray source, EDX detector and argon ion gun. They maximise the acceptance angle ($50^\circ$) to boost sensitivity and signal intensity. Additionally,
they can retard the electron kinetic energy to match that of the pass energy before reaching the analyser and finally they also control the area of the surface from which the electrons are collected.

![Figure 3.20 Schematic of a HSA and transfer lens system [64].](image)

### 3.2.3.8 Vacuum system

AES and XPS require UHV, this is in the range $1 \times 10^{-8}$ to $1 \times 10^{-10}$ mbar. As the analysis depth is so shallow any change to the surface over the analysis time will result in a poor spectral representation of the original sample surface. If a high vacuum system is used with an internal system pressure of $10^{-6}$ mbar, a monolayer of material is absorbed onto the surface within a few seconds. With analysis times of minutes to hours, in the case of SAM maps, the lowest pressures possible are desired to stop the build-up of absorbed contamination. UHV is also required as residual gas molecules in the analysis chamber causes scattering of the emitted electrons resulting in reduced signal intensity and more noise in the spectrum.

To achieve UHV the MICROLAB 350 uses a turbo molecular pump, backed by a roughing pump, which is connected to the entry lock, EX05 argon ion gun and EDX detector. It is initially used to reduce the main chamber pressure to $1 \times 10^{-7}$ mbar following instrument maintenance. The preparation chamber pressure is further reduced to $1 \times 10^{-8} - 10^{-9}$ mbar by an ion pump. The analysis chamber is also pumped by a large ion pump together with a sublimation pump to achieve a pressure of $1 \times 10^{-10}$ mbar, ensuring that the formation of a monolayer of adsorbed material takes several hours. In addition to these pumps the electron column and FEG are pumped by an additional small ion pump.

A turbo molecular pump works on the principle that when gas molecules are repeatedly hit by a moving surface they will gain momentum in the desired direction. The pump consists of a series of rapidly rotating turbine blades and counter rotating stator pairs, residual gas molecules preferentially collide with the underside of the blades and because the lower side faces down, the majority of gas molecules are scattered down into the pump and towards the exhaust. Gases that are captured by the upper stages of the pump are pushed into the lower stages where they are compressed to the backing pump pressure. A backing pump is
connected to the exhaust of the turbo pump which itself exhausts to atmosphere. A rotary pump is used for the purpose.

The sublimation pump or getter pump consists of three independent Ti-Mo alloy filaments bent into loops, held in a separate compartment below the analysis chamber. When a large current is applied to the filament it is heated and titanium vapour is released. The vapour condenses on the walls of the chamber forming a thin film. The thin film reacts with residual gas molecules in the chamber forming stable solid compounds that are not rereleased into the chamber atmosphere. The filaments are usually automatically fired in 60 second bursts every few hours to maintain the analysis chamber pressure. Three filaments are present as each is consumed after ~5 hours of constant use and replacement requires the instrument to be vented.

The ion pump consists of a stainless steel cylindrical anode and two titanium cathode plates, positioned at either side of the anode. The titanium cathode acts as the getter material just as in the sublimation pump. A high potential difference is applied causing the emission of electrons from the anode and the production of a magnetic field. The electrons ionise incoming gas molecules which are then accelerated into the cathodes. Upon impact the ions can become buried or can sputter small amounts of titanium cathode material into the pump. The sputtered titanium acts just as it does in the sublimation pump, forming thin layers that react with residual gas molecules.

3.2.4 Data interpretation

3.2.4.1 Spectra

There are three main features that are present in an Auger spectrum. These being the secondary electron tail, the Auger transitions and the backscattered electron peak. Figure 3.21 shows each of these from a steel sample. The backscattered peak is only observed when the primary beam energy is low. This is because as the analyser is not able to collect electrons with energies above ~2.5 keV.

Each element in the periodic table has a unique series of Auger transitions that can be used to identify it. Many elements display multiple transitions, some of which are more intense than others. For light elements the \( KL_{2,3}L_{2,3} \) transition is the most intense, except for beryllium for which it is the \( KL_{1,1} \). For slightly heavier elements, such as silicon, the \( KLL \) transition is usually used as the main peak for identification at ~1616 eV. However, the \( LMM \) transition is also present at 92 eV and is more intense but is often overlapped by other element transitions. Additionally, as the transition is so low in kinetic energy it is particularly surface sensitive and can be very weak for samples with a layer of hydrocarbon contamination.

The 3d transition metals show a characteristic triplet of \( LMM \) transitions, these being the \( L_3M_{2,3}M_{2,3}, L_3M_{2,3}M_{4,5}, \) and \( L_3M_{4,5}M_{4,5} \) peaks. The 4d transition metals show a sharp closely spaced doublet of the \( M_{4,5}N_{4,5}N_{4,5} \) transitions.
In addition to the Auger transitions, there are a number of fine features in the spectrum. These can be caused by chemical effects or from final state effects.

A chemical effect is the shift in kinetic energy that is observed in an Auger transition when analysing an element that has undergone a change in oxidation state. The peak will be shifted to a lower kinetic energy as the oxidation state of the element increases. The effect is usually only observed for elements which have a core-core-core (CCC) Auger transition, that is to say the Auger electron is generated from a core energy level of the element and not the valence band, where changes in the atomic environment are felt to a much lesser degree. For CCC Auger transitions, each of the three electrons involved in the Auger process originate in discreet energy levels and so the Auger electron produced has a well-defined kinetic energy. For core-valence-valence (CVV) Auger transitions, only the initial electron originates from a discreet energy level. The other two electrons are generated from degenerate valence electron orbitals with a range of energies. As such the Auger transitions produced will be a convolution of the valence band with a poorly defined kinetic energy.

Two examples of CCC transitions are shown in Figure 3.22. Beryllium and aluminium have thin oxide layers and high resolution analysis shows both oxide and metal peak components. For beryllium, the metal peak is observed at 102.5 eV and the oxide peak is observed at a lower kinetic energy of 94 eV, a shift of ~8 eV. For aluminium, the primary metal peak is observed at 1394 eV and the oxide at 1387 eV, a shift of ~7 eV. In the metal a higher kinetic energy is needed to eject the Auger electron as the nucleus is screened by the conduction band electrons. In an oxide, the metal atom is in a more electronegative environment, as electron density from the metal atom is lost to the oxygen atom. The result is less screening of the nucleus by the electrons and so less energy is required to eject an electron. This results in the oxide peak being shifted to a lower kinetic energy value than the metal peak.
Final state effects tend to have less of an impact on the appearance of the spectrum and only result in slight changes to the Auger peaks. They are most apparent in chemisorbed layers on a substrate. These occur after ionisation of the element, at which point the electron to fill the core hole does not come from an outer shell of the atom but from the valence band of the substrate. The result is that the main Auger peak is still observed in the characteristic region of the chemisorbed element but a slight shift of 1-2 eV is recorded in its kinetic energy.

Other features observed in Auger spectra are plasmon loss peaks. They can easily be confused with the fine structure of some Auger transitions. Shown in Figure 3.22 (b) is a bulk plasmon loss peak, at ~1377 eV, associated with the aluminium metal Auger transition, at 1394 eV. Plasmon loss peaks are of two types, surface and bulk. The peaks are produced by electrons as they exit the material and lose a discrete amount of their energy by exciting modes of collective oscillation in the conduction band electrons. Auger electrons which undergo this loss will generate a peak with energy as per Equation 3.7 [61]:

$$KE = E_{AES} - n \omega_b$$

Where:

n is the plasmon order and \( \omega_b \) is the oscillation frequency. In aluminium, this is approximately 15 eV for a bulk plasmon and 10.5 eV for a surface plasmon. In beryllium, these values are ~18 and 12.5 eV respectively. The energy of the surface plasmon is related to the bulk plasmon by Equation 3.8 [61]:

$$E_{Surface} \approx \frac{E_{Bulk}}{\sqrt{2}}$$

Plasmons have a range of specific frequencies each requiring an increasing amount of energy to excite, the first plasmon is denoted \( n = 1 \) and the second \( n = 2 \) and so on. Surface plasmons are weaker than bulk plasmons and fade into the noise quickly. Bulk plasmons are more intense and are easily identifiable in the spectrum of the backscattered electron peak until \( n = 7 \). Plasmons do not have much analytical purpose, other than an assessment of surface cleanliness in Auger analysis, they usually only complicate the interpretation of a spectrum.
An Auger spectrum can either be displayed in the direct form or in the differential form. In this work the direct form was used. The differential form can be used in order to help distinguish between peaks that strongly overlap. It is also useful for comparing older Auger data to modern data. A concern that occurs in the comparison between modern Auger data and older data is the shift in the zero kinetic energy position. Auger data in the past was referenced to the vacuum level while modern data is referenced, like XPS data, to the Fermi level [69]. The difference between them is the work function. The process of differentiating will also add ~5 eV to the peak position, which is taken as the minimum in the spectrum, as is shown in Figure 3.24. The old differential style of the displayed spectrum was a result of the phase sensitive detector (lock in amp) while to display the differential spectral form now a mathematical differentiation is performed on the data.

3.2.4.2 Scanning Auger microscopy

In Auger imaging, the intensity of a specific peak of nominated kinetic energy is collected as the electron beam is rastered over a selected area. The variation in the intensity between a peak and background is recorded and an image is produced that represents the surface distribution of an element. Individual maps are collected for each element of interest.
One of the primary decisions for SAM is whether a peak should be collected using serial or parallel acquisition. Each has their own advantages and disadvantages. In serial acquisition the energy range of an Auger peak is scanned across the channeltrons, just as in point analysis, all six channeltrons collect the spectrum from the background through the peak and back to background. The result is a high count rate where the presence or absence of a peak can be determined with near certainty. However, as the energy range of the peak has to be scanned for every pixel it results in an extremely slow mapping speed. At \(~10\) seconds per pixel a \(128^2\) map would take two days per element analysed. Although, with a stable sample and sufficient time for analysis serial acquisition results in maps of unsurpassed quality.

Parallel acquisition or snapshot mode is nearly always used instead of serial acquisition for SAM mapping. Here each channeltron collects only one kinetic energy of the spectrum. The result is a significant time saving, as the analyser does not need to scan the energy range of interest. A single pixel takes \(~0.1\) seconds to acquire a usable signal. Therefore, a \(128^2\) map would take 27 minutes per element to be analysed. A large drawback of this mode is the \(~100\times\) drop in signal intensity and so the presence of peaks is less certain. As such, it is good practice to back up elemental maps with point spectra to clearly show if an element is present.

The first step in Auger imaging is to find a suitable feature in the SEM. From this feature the SEM “register mode” is used to capture an image and save it to the computer memory in order to allow the software to perform a drift correction during AES mapping. This is performed by overlaying a new image over the original and shifting the electron beam such that the same features overlap if drift has occurred. When the area of interest is located a rectangular shape can be placed anywhere in the FOV or the whole SEM FOV may be used, where the beam will be rastered during the map acquisition. This area is then divided into a set number of pixels, were the beam will raster to collect Auger electrons. Ideally, to maximise the efficiency of data collection, the pixel size should match the electron beam spot size.

The resolution of the map can be selected from \(64\)-\(1024^2\) pixels. The choice is a compromise between resolution, image quality and acquisition time. Maps in this work were typically collected using aperture 4, with a beam energy of 10 or 15 keV, a beam current of 8-12 nA, FOV of \(~15\times15\ \mu\text{m}\) and a map resolution of either \(128^2\) or \(256^2\). If a map of \(512^2\) is selected for features of this size and pixel size is \(40\ \text{nm}\), then the individual pixel size is larger than the beam spot size resulting in lower quality mapping.

The next step in Auger microscopy is to select the regions of the spectrum that are of interest. This is achieved by using serial acquisition Auger point analysis to determine the elements present and the kinetic energy of the transitions of interest. For every peak of interest at least one kinetic energy representative of the peak energy and background energy have to be selected. The peak intensity is the difference between the intensity measured at the peak maximum \((P)\) after subtracting the intensity at the background \((B)\).
The MICROLAB 350 has six channeltrons which are used for parallel acquisition of Auger maps. The retard ratio that is typically used for SAM is 2.8. This is used instead of 4, which is usually used for point analysis, to increase the signal intensity. As the kinetic energy increases and the pass energy increases the energy window that the channeltrons collect get broader. This can cause a problem in the acquisition of low energy transitions such as Be KLL as the energy window at 100 eV, is only 3.7 eV using a retard ratio of 2.7, while the peak itself is ~5 eV wide. Therefore, the channeltron energy window is too narrow for the detector to effectively map the peak and either the retard ratio must be reduced further or a map can be collected using serial acquisition. At high kinetic energy some peaks such as Al KLL at 1400 eV, which will have an energy window of 52.1 eV, are too narrow to be mapped using all of the channeltrons. In this case only a few of the channeltrons are used to collect the peak with others turned off. The width of the energy windows was determined by the data acquisition software.

Depending upon the shape and width of the Auger transition the channeltrons can be assigned to either the peak or background positions in the spectrum or they can be turned off. Figure 3.25 shows an example of how the channeltrons are assigned for the O KLL peak at 506 eV. A suitable assignment sequence would be POOBBB. Where P = peak, O = off and B = background. Using a retard ratio of 2.8 the energy width on the channeltrons is about 20 eV at this kinetic energy.

![Figure 3.25 Example of the arrangement of the channeltrons used to acquire the peak and background intensities of an O KLL transition.](image)

The elemental maps produced in SAM are typically presented after processing the data to remove the influence from topographic effects in the image. This is performed because areas facing the analyser will have greater signal intensity than areas facing away from the analyser. Figure 3.26 shows an example of O KLL maps generated using different algorithms. If the peak intensity (P) is used for the Auger map, an image similar to the SEM micrograph of the surface is produced. This is because the yield of Auger electrons as well as secondary electrons is increased from areas of higher atomic mass and with steeper topography. The effect of increased signal intensity resulting from the topography around the rim of the feature in the map for the P-B map is clearly evident. There is only a slight difference in contrast between the two algorithms (P-B/B) and (P-B/P+B).
3.2.5 Quantification in Auger electron spectroscopy

3.2.5.1 Background

During this PhD the opportunity to collaborate with the University of Southampton Optoelectronics research department presented itself. This took the form of performing quantification on silicon and germanium alloy microelectronic devices using Auger electron spectroscopy. It was agreed to undertake this work as a learning exercise.

Quantification in AES is not typically carried out as a consequence of the difficulty in obtaining results of high accuracy. Matrix effects and backscattered effects can severely influence the quantification results obtained by the typically used methods. A simple linear expression where peak intensity is proportional to the molar fraction of a constituent element is usually used as the starting point for quantification. This is shown in Equation 3.9 [61]:

\[ X_A = \frac{I_A}{I_A^\infty} \]  

(3.9)

Where:

\( I_A \) is the peak intensity of element A, \( X_A \) is the molar fraction and \( I_A^\infty \) is the peak intensity from a sample of pure element A.

A more useful form of the equation for a binary alloy is shown in Equation 3.10:

\[ X_A = \frac{I_A/I_A^\infty}{\sum_{i=A,B} I_i/I_i^\infty} \]  

(3.10)
The use of this equation results in the production of a graph with a linear relationship between the intensity of material “A” in pure form to the intensity of material “B” in pure form. This equation ignores an important consideration for the quantification of samples, this being the presence of a possible matrix effect [61]. For some binary alloy systems a matrix effect is not observed and the above equation works well. However, for most binary systems this is not the case. A matrix effect is the influence of surrounding material on the signal of a chosen element. The effect can either have a positive or negative effect on the signal intensity.

A backscattering effect is also known to occur in materials and have an impact on the intensity of a given Auger transition. As the incident electrons interact with the surface they are scattered into the sample surface and also back out of the surface, on their way back out of the surface the backscattered electrons are able to excite Auger electrons. This effect is always present when an electron beam strikes a surface and results in the analysis spatial resolution of Auger spectroscopy always being slightly larger than the imaging spatial resolution in the SEM. The higher the atomic mass of the surface elements the greater this backscattering of the primary electrons. These backscattered electrons increase the Auger electron yield from the surface.

3.2.5.2 Determination of a matrix factor

By maintaining the same spectrometer settings for each analysis, together with the use of material standards, that represent a range of mixed concentrations of the elements of interest, it is possible to construct a plot to examine if a matrix effect is present. This effect, if present, can then be accounted for, using a correction called the matrix factor, when a sample containing the same elements but with unknown concentrations is analysed.

To determine if a matrix effect was present in the Si-Ge binary alloy system, four standard samples of known composition were analysed. These were: 52.4 at.% germanium and 77.5 at.% germanium purchased from IHP-microelectronics in Germany, together with >99.999 at.% silicon and >99.999 at.% germanium. Each sample was analysed at eight different points from across the sample surface. At each point the intensity of the Si KLL and the Ge LMM Auger transitions were acquired.

The presence of a matrix effect within the alloys was observed. The matrix effect is clear because the plot of the Si KLL and Ge LMM intensities does not show a linear relationship. The plot is shown in Figure 3.27. The deviation in intensity from the linear relationship is the result of a matrix effect within the samples. The result of the matrix effect is that as the concentration of germanium increases the intensity of the Si KLL does not decrease linearly in intensity.
By combining the known concentrations of the SiGe samples with the measured intensities of the Auger transitions, a matrix factor can be calculated using Equation 3.11:

$$\frac{x_A}{x_B} = F_{AB} \frac{I_A/I_A^\infty}{I_B/I_B^\infty} \quad (3.11)$$

An example calculation using Equation 3.11 to determine the matrix factor is shown below for the 52.5 at.% germanium alloy:

$$\frac{47.5}{52.5} = F_{AB} \frac{5791/13356}{12690/27746}$$

$$F_{AB} = \frac{47.5/52.5}{5791/13356/12690/27746} = 0.954$$

Ideally further standards should be analysed to investigate if the average matrix factor of 0.9 was representative of the entire concentration range. This value was in agreement with literature values [70].

Table 3.4 Calculated matrix factors for the two standard SiGe samples together with the average matrix factor

<table>
<thead>
<tr>
<th>Si at.%</th>
<th>Ge at.%</th>
<th>Calculated matrix factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>47.5</td>
<td>52.5</td>
<td>0.95</td>
</tr>
<tr>
<td>22.6</td>
<td>77.4</td>
<td>0.85</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>0.90</td>
</tr>
</tbody>
</table>

### 3.2.5.3 Use of the matrix factor to determine the concentration of silicon and germanium in microelectronic devices.

This work was carried out as part of a collaborative effort with the Optoelectronics Research Centre at the University of Southampton. The aim of the investigation was to compare the elemental concentrations along a single strip, silicon-germanium on insulator (SGOI) device, shown in Figure 3.28, to that of the centre strip from a tree-like, branched structure, shown in Figure 3.31. The devices were analysed using AES point spectra. The intensities of the silicon and germanium peaks were recorded following a linear background.
subtraction over the energy ranges 1300-1650 eV and 650-1205 eV for the Si \textit{KLL} and Ge \textit{LMM} Auger transitions respectively.

An example calculation, using the previously determined matrix factor of 0.9 and Equation 3.11, is shown below for “point 2” on the single strip device. Table 3.5 and Table 3.6 show the concentrations found using this calculation for each of the points from the single strip and the branched structure.

Point 2 quantification

\[
A = \text{Si}, \quad B = \text{Ge} \\
\frac{X_A}{X_B} = 0.9 \frac{9669/13356}{8346/27746} \\
\frac{X_A}{X_B} = \frac{0.6515}{0.3001} \\
X_A + X_B \equiv 100 \\
X_A = X_B \left( \frac{0.6515}{0.3001} \right) \\
100 = X_B + X_B \left( \frac{0.6515}{0.3001} \right) \\
100 = \frac{X_B}{0.3001} + \frac{0.6515X_B}{0.3001} \\
100 = \frac{0.9515X_B}{0.3001} \\
30.01 = 0.9515X_B \\
\frac{30.01}{0.9515} = X_B \\
X_A = 68.5\% \quad X_B = 31.5\% 
\]

The strip shown in Figure 3.28 was analysed using eleven AES points. These took into account the full length of the strip together with the silicon dioxide substrate and the silicon seed crystal.
Figure 3.28 SEM micrograph of the 100 µm strip device analysed by AES. Two images have been merged as the strip was too long for a single SEM FOV at the desired magnification.

Figure 3.29 shows the high resolution spectra collected from "Point 2" on the strip, shown in Figure 3.28, which is located four micrometres from the start of the strip and overlaps the region where the strip meets the silicon seed crystal. (a) Shows the intense Si KLL Auger transition and (b) shows the less intense Ge LMM Auger transition. Figure 3.30 shows the AES spectra collected from "Point 10" of the strip, shown in Figure 3.28, which is located 94 micrometres from the start of the strip. (a) Shows the weak Si KLL Auger transition and (b) shows the more intense Ge LMM Auger transition. The spectra show that the concentration of silicon and germanium are not constant along the length of the strip as the intensities of the peaks changes significantly at each end.

Figure 3.29 High resolution spectra from “Point 2” located four micrometres from the start of the strip and overlapping the region where the strip meets the seed crystal. (a) Si KLL Auger transition and (b) Ge LMM Auger transition.
Figure 3.30 High resolution spectra from “Point 10” located 92 µm from the start of the strip. (a) Si KLL Auger transition and (b) Ge LMM Auger transition.

Shown in Table 3.5 are the peak intensities for the Si KLL and Ge LMM Auger transitions from each point along the strip device. The silicon intensity was found to decrease and the germanium intensity increase moving along the strip. The calculated concentrations from these intensities are also shown in the table. These reveal that the concentration of silicon is not constant along the strip and gradually falls to ~5 at.%.

<table>
<thead>
<tr>
<th>Point on strip</th>
<th>Ge intensity (counts s⁻¹)</th>
<th>Si intensity (counts s⁻¹)</th>
<th>Si at.%</th>
<th>Ge at.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>14606</td>
<td>100.0</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>8346</td>
<td>9669</td>
<td>68.4</td>
<td>31.6</td>
</tr>
<tr>
<td>3</td>
<td>26814</td>
<td>5049</td>
<td>26.1</td>
<td>73.9</td>
</tr>
<tr>
<td>4</td>
<td>28036</td>
<td>4335</td>
<td>22.4</td>
<td>77.6</td>
</tr>
<tr>
<td>5</td>
<td>31417</td>
<td>4312</td>
<td>20.4</td>
<td>79.6</td>
</tr>
<tr>
<td>6</td>
<td>30921</td>
<td>1369</td>
<td>7.7</td>
<td>92.4</td>
</tr>
<tr>
<td>7</td>
<td>30620</td>
<td>1361</td>
<td>7.7</td>
<td>92.3</td>
</tr>
<tr>
<td>8</td>
<td>31171</td>
<td>903</td>
<td>5.1</td>
<td>94.9</td>
</tr>
<tr>
<td>9</td>
<td>31905</td>
<td>759</td>
<td>4.3</td>
<td>95.7</td>
</tr>
<tr>
<td>10</td>
<td>31583</td>
<td>1011</td>
<td>5.7</td>
<td>94.4</td>
</tr>
<tr>
<td>11</td>
<td>0</td>
<td>13939</td>
<td>100.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Use of a branched structure was believed to enable the tailoring of the silicon and germanium concentrations along the central strip. Figure 3.31 shows the branched structure that was analysed using eight AES points. The eight points were positioned to avoid regions damaged by previous analysis of the sample using Raman spectroscopy, by Southampton University. Each analysis position was between the side branches and covered the entire length of the central strip. The seed crystal is located off of the right hand side of the SEM FOV.

Figure 3.32 shows the high resolution Si KLL (a + c) and Ge LMM (b + d) Auger transition regions collected from "points 1 and 8" of the tree structure. The spectra show that the intensities of the Auger transitions are approximately the same at both ends of the central strip, compared to the large difference that was observed for the singular strip without branches.
Figure 3.31 SEM micrograph of a SGOI device with a branched structure.

Figure 3.32 High resolution spectra from "Points 1 and 8" along the central strip of the tree like device. (a) Si KLL and (b) Ge LMM from "Point 1", (c) Si KLL and (d) Ge LMM from "Point 8".

Shown in Table 3.5 are the peak intensities for the Si KLL and Ge LMM Auger transitions from each of the eight points along the central strip of the branched device. The silicon and germanium peak intensities were found to be fairly constant along the strip. The calculated concentrations from these intensities are also shown in the table showing that, within ~5 at.%, the concentration of silicon and germanium was constant along the length of the device.
Table 3.6 Auger peak intensities of the Ge LMM and Si KLL transitions, following linear background subtraction from the central strip of the branched structure together with their calculated concentrations

<table>
<thead>
<tr>
<th>Point</th>
<th>Ge intensity (counts s$^{-1}$)</th>
<th>Si intensity (counts s$^{-1}$)</th>
<th>Si at.%</th>
<th>Ge at.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25844</td>
<td>3350</td>
<td>19.5</td>
<td>80.5</td>
</tr>
<tr>
<td>2</td>
<td>26397</td>
<td>3207</td>
<td>18.5</td>
<td>81.5</td>
</tr>
<tr>
<td>3</td>
<td>29722</td>
<td>3073</td>
<td>16.2</td>
<td>83.8</td>
</tr>
<tr>
<td>4</td>
<td>30297</td>
<td>2895</td>
<td>15.2</td>
<td>84.8</td>
</tr>
<tr>
<td>5</td>
<td>29502</td>
<td>3000</td>
<td>16.0</td>
<td>84.0</td>
</tr>
<tr>
<td>6</td>
<td>29573</td>
<td>2992</td>
<td>15.9</td>
<td>84.1</td>
</tr>
<tr>
<td>7</td>
<td>29564</td>
<td>3197</td>
<td>16.8</td>
<td>83.2</td>
</tr>
<tr>
<td>8</td>
<td>28935</td>
<td>2875</td>
<td>15.7</td>
<td>84.3</td>
</tr>
</tbody>
</table>

Figure 3.33 shows a comparison between the SiGe composition in the centre strip of the branched structure and that of the straight strip, as collected by AES and Raman. The concentrations measured using each technique showed the same trend. The single strip showed a gradual decay in the concentration of silicon with distance from the seed crystal. While the concentration of silicon in the central strip of the branched structure remained relatively constant. This trend was observed in the data from Raman and AES. The Raman was performed by collaborators at the University of Southampton [71]. The analysis proved that the addition of the side branches to the strip devices successfully produced a strip with constant composition.

![Graph of the Auger and Raman data collected from the strip and branched, tree-like devices.](image)

3.2.5.4 Problems with quantitative analysis for materials in this project

The main aim of this work was to gain a further understanding of the microchemistry associated with the second phases present in beryllium, the majority of which are known to consist of two or more elements [16]. Auger quantification cannot reliably be performed on samples without the use of standards with known concentrations to take account of possible matrix and backscattered effects. As such, to perform reliable quantification of beryllium inclusions materials of known composition would be required. Materion Brush was approached during this project to produce a range of beryllide standards but the costs of producing one off materials was far too high for them to consider. Therefore, without the use of suitable standards, quantification of beryllium using AES was not attempted during this work.
### 3.3 Energy dispersive x-ray spectroscopy

#### 3.3.1 Background

As previously described in the AES section, bombardment of surface atoms with primary electrons causes the ejection of core electrons, resulting in excited atoms that can undergo relaxation through the competing processes of Auger electron or x-ray emission. In each case, the emitted energy is characteristic of the electron orbitals of the excited atom and so can be used analytically to determine the sample composition. Figure 3.34 shows a schematic to illustrate where two common x-ray transitions used for elemental identification are generated from within the electron orbitals of an atom.

Unlike in XPS and AES where the analysis depth is determined by the attenuation length of the emitted electrons, in EDX the analysis depth is primarily dependent upon the interaction/scattering volume of the incident electrons. In EDX, the analysis depth is typically taken as the total interaction volume of the primary electron beam within the sample surface. This is because the attenuation length of x-rays within a material is much greater than electrons of the same kinetic energy, in the range of micrometres compared to nanometres. This is not always the case and many examples of the depth of analysis being limited not by the depth of generated x-rays but by the attenuation length of x-rays exist. This is particularly true for low energy x-rays in a dense material. More details on this effect are described in Chapter 5.

![Figure 3.34 Schematic of the electron orbitals involved in the generation of Kα and Lα x-ray transitions, which are usually used in EDX analysis.](image)

#### 3.3.2 EDX detectors

##### 3.3.2.1 Silicon lithium detector (SiLi)

The SiLi x-ray detector consists of a piece of semiconducting silicon doped with trace levels of lithium which is arranged in a p-i-n junction. It is held between two thin layers of gold at both surfaces held at opposite potentials, as shown in Figure 3.35. When an incoming x-ray photon collides with the silicon a number of electron-hole are generated. The creation of an electron-hole pair requires 3.8 eV, it follows that the number of pairs generated is proportional to the energy of the x-ray photon. By applying a voltage across the gold layers, the creation of the electron-hole pairs by the x-ray causes a small current to flow. The detector is cooled using liquid nitrogen to -196 °C, in order to increase the resistivity of the silicon. If the
conductivity of the silicon is too high then electrons can become trapped at the edge of the silicon and the detected charge is smaller than that generated by the x-ray. This results in additional noise in the spectrum.

![Figure 3.35 Schematic of a silicon lithium energy dispersive x-ray detector [72].](image)

To protect the sensitive detector from contamination, which can affect the detectors performance, a window of beryllium (~7 μm thick), or a polymer membrane (<0.5 μm) is fitted between the detector and the main analysis chamber. Unfortunately, use of a window has the effect of absorbing a proportion of low energy x-rays, making light elements more difficult to detect. Older beryllium windows are now being replaced by polymer windows that can be made much thinner and result in higher low energy x-ray transmission. Figure 3.36 shows the transmission of x-ray photons in a SiLi detector with various window types. The increase in the transmission of low energy x-rays is significant when the thick beryllium window is replaced with thinner polymer windows.

![Figure 3.36 Absorption effects with an EDX detector using various window designs [73].](image)

### 3.3.2.2 Silicon drift detector (SDD)

The older SiLi detectors have largely now been replaced with silicon drift detectors (SDD). Both types of detector were utilised during this project. Drift detectors have a much lower capacitance than a planar detector of the same area, resulting in less noise in the spectrum, allowing for higher count rates and improved spectral resolution. Figure 3.37 shows a schematic for the structure of a drift detector. It consists of a series of biased field strips which produce a radial electric field. The field guides the electrons generated
from an x-ray strike to the anode in the centre, which is connected to a field effect transistor where the signal current is collected. As the electrons are guided to the anode from anywhere within the silicon, the anode can be made smaller, lowering the anode capacitance and reducing noise.

Figure 3.37 Schematic of a silicon drift energy dispersive x-ray detector [74].

SDDs offer a number of advantages over SiLi detectors: the first of these is higher low energy x-ray transmission. Just like SiLi detectors the sensitive x-ray detector in a SDD is isolated from the main analysis chamber to prevent contamination. The SDD and the SiLi detectors used in this project both use a polymer window instead of beryllium. This results in greater transmission of low energy x-rays. Figure 3.38 shows and expanded low energy view of an EDX spectrum collected from a beryllium specimen using a SDD. It shows that the transmission of low energy x-rays is sufficient to observe the Be Kα peak separated from the x-ray noise peak.

Figure 3.38 Expanded view of an EDX spectrum collected from a beryllium sample using a SDD.

Another significant advantage of SDDs over SiLi detectors is the count rate. SDDs are capable of storage rates exceeding 750,000 counts s$^{-1}$, compared to SiLi detectors which tend to peak at ~140,000 counts s$^{-1}$. As well as the significant increase in bulk count rate, drift detectors also provide an improvement in the spectral line width over the entire count range of a SiLi detector and beyond. As shown in Figure 3.39 the Mn Kα FWHM is not significantly affected until counting over 220,000 counts s$^{-1}$. A count rate exceeding 10,000 counts s$^{-1}$ in a SiLi detector results in a significant loss of spectral resolution. At 140,000 counts s$^{-1}$ the resolution of Mn Kα is reduced from 129 eV to 195 eV compared to the SDD, which never reaches this value. Even at the maximum count rate the resolution is still 175 eV in a SDD.
Another advantage is the elimination of the requirement for liquid nitrogen cooling. Less noise is generated using the more stable SDDs and so they can be operated at higher temperatures (~20 °C). This can be achieved using a Peltier (thermoelectric) device with cooling fins attached to the detector.

### 3.3.3 Spectral interpretation

#### 3.3.3.1 Effects in the spectrum

The current produced by the x-rays striking the detector is referred to as pulse, as this current is so small it is amplified before being sent to the multichannel analyser. Depending upon the size of the current and hence the x-ray energy, the analyser will assign a channel for that signal adding an additional count to that energy channel. The channels are typically 15-20 eV wide. It is important that the analyser finishes counting the first pulse before it starts to try and count and assign the energy of the next. The speed with which the analyser can assign the pulses determines the rate at which x-rays can be counted. The total elapsed time for an EDX spectrum to be acquired consists of live time and dead time. The live time is the time spent counting pulses and the dead time is the time where the analyser must ignore pulses in order to prevent piling up of counts. The time taken to assign the pulses to a channel is known as the time constant.

For a good quality spectrum, that provides high energy resolution, it is best to use a long time constant, such as 50 or 100 μs. This gives the analyser enough time to assign the pulse to the correct energy channel, ensuring that the FWHM of the peak is close to the analyser resolution. The dead time in this case is then around 30%. When the maximum count rate is required, such as in the acquisition of EDX maps, a very fast time constant is used, such as 2-10 μs. This gives a large boost to the count rate but because the analyser is being bombarded with so many pulses the dead time increases to around 60%. As the analyser does not have sufficient time to assign the correct channel to the pulse, broadening of the peaks occurs. The shortest time constants are used in mapping and can result in peaks with a FWHM of ~170 eV while the longest time constants give peaks with a FWHM close to the analyser resolution of 130 eV.
The natural line width or the FWHM of an x-ray peak is energy dependent and is usually between 0.5-10 eV. Unfortunately, the FWHM of x-ray peaks in EDX is significantly degraded by the convolution of the detector-system response function. This has the disadvantage that distinguishing between close peaks or overlapping peaks is difficult. This is of great concern at the low energy region of the spectrum below ~1.5 keV. In this region the Kα x-ray lines of light elements and the La x-ray lines of heavier elements tend to severely overlap. For the analysis of low energy peaks, a long time constant should be used to achieve the best spectral resolution.

Two effects that can add to the confusion in the interpretation of spectra are sum peaks and silicon escape peaks. A sum peak occurs when two x-rays of the same energy enter the detector at the same time. The detector then interprets the signal as one x-ray of double the energy, this is observed in the EDX spectrum shown in Figure 3.40. Here, two Al Kα x-rays, of energy 1.48 keV, are summed and form a peak at 2.96 keV. This effect is usually observed for elements which are present at high concentrations. Silicon escape peaks are less commonly observed than sum peaks and are small peaks located 1.74 keV below a main peak. They are produced when an incoming x-ray has sufficient energy, usually >5 keV, to eject a K-shell electron from the silicon atoms in the x-ray detector. The original x-ray is then reduced in energy by 1.74 keV and a loss peak is observed.

![Figure 3.40 EDX spectrum of a 7075 aluminium alloy surface. An aluminium sum peak is observed at 2.96 keV, twice the x-ray energy of Al Kα 1.48 keV.](image)

### 3.3.3.2 Bremsstrahlung background

Bremsstrahlung or braking radiation x-rays are produced as the primary beam electrons slow down when they enter a solid. As shown in Figure 3.41 the primary electrons, (with energy \(E_0\)) lose some energy as a consequence of inelastic scattering caused by the interaction of the electron with the electrons surrounding the atoms in the sample. The energy that is lost to the atom is converted into x-rays which have a wide range of energies (\(E_i\)). The kinetic energy of the primary electron can be lost in a single interaction or through a series of interactions, where small proportions of the primary energy are lost. The gradual loss of energy through many steps is more likely, producing x-rays with energy >\(E_0\), which is why the x-rays are referred to as a continuum or background. The x-rays can have an energy from 0 to <\(E_0\) as primary electrons lose almost
no energy or lose almost all of their energy. The x-rays cannot have energies greater than or equal to the primary beam energy, this energy limit is known as the Duane-Hunt limit [76].

Figure 3.41 Schematic to show how the Bremsstrahlung radiation is produced [77]. Although a large number of low energy x-rays are generated, the majority are absorbed in the sample, this results in a large difference between the generated Bremsstrahlung x-ray spectrum and the observed Bremsstrahlung x-ray spectrum. This is shown in Figure 3.42.

Figure 3.42 Spectra of the Bremsstrahlung background shapes produced by (a) an electron beam striking a sample and (b) the actual detected background.

For samples containing elements with large x-ray cross sections the background is less significant and does not affect the interpretation of the spectrum. Figure 3.43 shows the EDX spectra collected from a steel sample using a range of primary beam energies. They show how the Bremsstrahlung background increases as the primary beam energy increases.
Figure 3.43 EDX spectra of a stainless steel sample collected using multiple beam energies with the increasing Bremsstrahlung background highlighted.

However, for light elements, with low cross sections, the background has a dramatic effect on the spectrum and can make spectral interpretation more difficult. An example of this is shown in Figure 3.44, which shows an EDX spectrum collected from a beryllium sample using a 15 keV primary beam energy. The background dominates the appearance of the spectrum. Low concentrations of aluminium, silicon and iron are present and the Al and Si Kα peaks together with the Fe Lα are superimposed on a steep background. Without the Fe Kα transition it would be difficult to determine if iron was actually present in the metal as the background is so high surrounding the Fe Lα.

Figure 3.44 EDX spectrum collected from beryllium using a 15 keV primary beam energy.

3.3.4 Depth of analysis

The volume of the primary beam interaction varies significantly according to the electron beam energy and the atomic mass of the material being analysed. Figure 3.45 shows a typical example of the sampling depth of AES compared with EDX. While Auger electrons escape from only the surface of the material, the x-rays used for EDX analysis escape from much deeper in the sample.
While it is often quoted that the interaction volume of EDX is about 1 µm$^3$, this is usually only the case when working with first row transitions metals at an operating potential of 20 kV. Figure 3.46 shows a comparison between the primary beam interaction volumes of (a) beryllium, showing a total interaction depth of 5 µm and (b) iron showing an interaction depth of ~1 µm. Inelastic scattering of the primary electrons lowers their kinetic energy as they travel through the analysed material, as such by the time they reach their maximum depth of penetration their kinetic energy is insufficient to excite most x-ray transitions. This is highlighted by the labelled contours in the figure. These are the regions at which the electrons only have certain percentage of their original kinetic energy remaining. The large difference in the depth of x-ray generation and x-ray emission is further investigated in Chapter 5.

**Figure 3.45 Schematic to of the characteristic analysis depths in EDX and AES.**

**Figure 3.46 Monte-Carlo simulations using Win X-ray software [78], of primary electron beam interaction depths with (a) beryllium and (b) iron substrates using a 20 kV beam. Both are plotted on the same scale.**

### 3.3.5 Quantitative analysis

The relative intensity of an x-ray peak is proportional to the atomic mass and concentration of the element. This is because the mass of the material through which the primary beam can penetrate is approximately equal for all elements as the primary electrons are retarded by interactions with sample electrons, which scales with the atomic mass of the material. By using material standards of a pure element or compound the concentration of an element can be approximately determined using Equation 3.12:
\[ C' = \left( \frac{I_{sp}}{I_{st}} \right) C_{st} \]  

(3.12)

Where:

- \( C' \) is the concentration in the material,
- \( I_{sp} \) and \( I_{st} \) are the intensities measured from the sample and standard respectively,
- \( C_{st} \) is the concentration of the element in the standard.

However, in order to obtain more rigorous quantification in EDX a number of effects must be taken into account. Background subtraction is performed on the EDX peaks to obtain a more accurate value of the intensity of the integrated peak area. As the peaks tend to be quite broad, their tails interfere with the surrounding background making it difficult to find a suitable region near the peak to perform a background subtraction. Contributions from the Bremsstrahlung background must also be accounted for. The most common way to account for this is with a mathematical function that combines information on the elements together with a detector response function to calculate a theoretical background for the sample which can then be subtracted.

This effect is important in the production of EDX element count maps. When a map is produced from the raw counts, any counts in the energy channels allocated to a particular element are assigned to the map of that element. This has the effect of counting noise as part of the peak. For example, by mapping the Cr Kα transition, any x-ray that is assigned to an energy channel between 5279 eV and 5545 eV will be counted as a chromium x-ray and added to the map. This includes any x-rays from the background. Performing a background subtraction results in x-ray maps in which the counts that are assigned to a map must have originated from a peak above the background. This has the effect of removing a significant amount of noise from the maps, providing a more accurate representation of the distribution of the element in the sample.

An example of a Cr Kα x-ray map, produced using counts (a) and net counts (b), is shown in Figure 3.47. It shows how a significant amount of noise has been removed from the map when it is displayed in the net count form. The area surrounding the intermetallic does not contained a detectable concentration of chromium and this is most accurately reflected by the net counts map.

![Figure 3.47 Chromium x-ray maps from an intermetallic in aluminium, processed displayed in: (a) raw counts and (b) net counts.](image-url)
Matrix corrections must be applied. These correct for the type of environment the element of interest is in within the sample. The first part of the correction is referred to as the stopping power correction. This accounts for the differences in the sample mass analysed as it is not constant. The second part is the backscattering correction. This accounts for the backscattered electrons that elastically exit the sample and do not excite x-rays. The third part accounts for fluorescence corrections. These corrections are needed as it is possible for the enhancement of some x-ray lines to occur as a result of fluorescence by other x-rays generated in the sample by higher energy x-rays. For example, the Fe Kα x-ray at ~6.4 keV, has more than enough energy to excite the O Kα transition at ~0.5 keV. Without the correction, the concentration of oxygen, as found by performing quantification on the spectrum, would be higher than it really is in the sample.

The fourth part considers the attenuation of x-rays within a sample. Some samples absorb x-rays highly, like gold, while others only lightly, like beryllium. The absorption correction is considered the most important and it is dependent on the emission angle of the x-rays to the x-ray detector. This angle is the x-ray take off angle as measured from the sample normal and is usually 50° or 40° from the sample surface.

Correcting the quantification for these effects is known as the ZAF correction. (Z) represents the atomic number effects, (A) the absorption effects and (F) the fluorescence effect.

The minimum detectable concentration (MDC) of a particular element depends upon how well the x-ray peak rises from the background. The concentration is initially calculated using a pure standard, as per Equation 3.13:

$$MDC = \frac{200\sqrt{b}}{(p-b)\sqrt{t}}$$ (3.13)

Where:

$p$ is the peak counts $s^{-1}$ from a standard, $b$ is the background counts $s^{-1}$ and $t$ is the analysis time, in seconds. Increasing the time of analysis will decrease the MDC, the smallest detectable peak is $2\sqrt{(bt)}$. The detection limit for most transition metal elements is typically about 0.5 at.% but it can be considerably higher for light elements.

### 3.4 Wavelength dispersive x-ray spectroscopy

Wavelength dispersive x-ray spectroscopy (WDX) is similar to EDX, the sample surface is bombarded with electrons and x-rays are emitted. These x-rays are counted at the detector and an energy spectrum is built up. The difference between EDX and WDX is that in WDX the x-rays emitted from the sample surface are first diffracted through a crystal before reaching the detector. The basic principles of WDX are based on Bragg’s Law, as shown in Equation 3.14:

$$n\lambda = 2d \sin \theta$$ (3.14)
Where:

n is an integer, \( \lambda \) is x-ray wavelength in nanometres, d is the lattice parameter of the diffracting crystal and \( \theta \) is the angle of angle of incidence of the x-ray.

The energy of the x-ray is found using Equation 3.15:

\[
E(keV) = \frac{1.2398}{n\lambda} \text{ or } E(keV) = \frac{1.2398}{2d \sin \theta}
\]  

(3.15)

The energy of the x-ray, as measured by the detector, is determined by the value n or 2dsin\( \theta \). As “n” can be any integer, it is possible to observe higher order x-ray reflections. If the detector is sensitive enough, \( n = 2 \) and even \( n = 3 \) can be observed, although the peak intensity falls away dramatically for the higher order lines. These are observed at a half and a third of the primary x-ray peak energy, respectively. Their presence usually acts to hinder analysis as they can be mistaken for other elemental peaks. These higher order lines are further discussed later.

A Thermo Scientific MagnaRay spectrometer was used in this work. The spectrometer is fitted with six x-ray diffracting crystals. Four of these crystals are part of the standard configuration offering diffraction through the energy range 0.16-12 keV, while two are additional crystals added depending upon the customer requirements. In this system the MoB4C and WSi60 crystals were added. These provide improved resolution for the analysis of beryllium, carbon and oxygen in the energy ranges 65-255 eV and 215-850 eV. The various crystals and their diffraction energy ranges are shown in Table 3.7.

<table>
<thead>
<tr>
<th>Diffractor</th>
<th>Energy range (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoB4C</td>
<td>65-255</td>
</tr>
<tr>
<td>NiC80</td>
<td>160-640</td>
</tr>
<tr>
<td>WSi60</td>
<td>215-850</td>
</tr>
<tr>
<td>TAP</td>
<td>500-1,990</td>
</tr>
<tr>
<td>PET</td>
<td>1,470-5,800</td>
</tr>
<tr>
<td>LiF (200)</td>
<td>3,200-12,000</td>
</tr>
</tbody>
</table>

X-rays generated from the sample diverge out from the surface in all directions. A conventional WDX system is based upon a Rowland circle. The sample, diffracting crystal and the detector must all be placed on a circle to satisfy Bragg’s law. The detector must move around the circle in order to collect x-rays of different energies, the requirement for the circle results in a bulky detector system. Figure 3.48 shows the setup for a Rowland circle WDX system. The yellow hemisphere shows the entire region of emitted x-rays, the blue cone represents the x-rays that reach the diffracting crystal and the red cone represents the x-rays diffracted onto the detector. The drawback of the Rowland circle WDX system is the small cone angle of x-rays that reach the detector.
The WDX detector used in this work was a parallel beam system. An example of a parallel beam WDX system is shown in Figure 3.49. In parallel beam WDX, an x-ray optic is brought close to the sample surface. By bringing a collimating optic close to the surface, the divergent x-rays from a large cone angle are transformed into a parallel beam to reach the detector. Not only is the cone angle and hence the number of x-rays collected from the sample surface greatly increased with a parallel angle system but the detector does not need to move. Instead the diffracting crystal rotates to collect different energy x-rays.

The greatest benefit of WDX compared to EDX is the large reduction in the full width half maximum for the peaks of interest. While an EDX detector is typically rated to ~128-150 eV FWHM for the Mn Kα transition, this is much reduced in WDX, with typical resolutions of 1-30 eV. As the x-rays are diffracted through the chosen crystal only those of the exact energy to satisfy Bragg’s law are diffracted constructively to the x-ray detector. Figure 3.50 shows an example of the resolution achieved with EDX, recorded with the longest time constant (smallest FWHM) and with WDX, from a Kovar sample. The FWHM of the Fe Lα WDX peak was measured as 5 eV. However, in order acquire such a wide energy range the step size was set as 5 eV and so the FWHM was limited by this choice and not by the detector or the x-ray line width. The detector is capable of collecting x-rays with a 0.1 eV step size which would reduce the FWHM considerably, although this increases the acquisition time accordingly. The FWHM for the Fe Lα as measured by EDX was 150 eV.
Diffraction through the WDX crystals does not remove the Bremsstrahlung background in a spectrum. This is because the entire x-ray energy range is diffracted through the crystal sequentially. However, the signal to noise is significantly improved for peaks, resulting in increased elemental sensitivity. Figure 3.51 shows the entire x-ray energy range for a Kovar sample analysed using WDX. The black arrows show sudden jumps in the background intensity as the spectrometer switches between the various diffracting crystals. As a crystal reaches the end of the energy range it can diffract, it becomes more imperfect at diffracting. Bragg’s law becomes less satisfied and more x-rays are transmitted through the crystal. The diffracting efficiency of the next crystal is considerably improved compared to the last part of the previous crystal, resulting in the transmission of fewer x-rays and a lower background. This is observed in the spectrum a number of times, as crystals are switched to collect a large energy range. It is possible to actively choose which crystal to use in the energy regions where two crystals can diffract the same energy range. In this case, the lower energy crystal will be used to maximise intensity and the higher energy crystal used for resolution. Second order, \( n = 2 \), reflections for the Fe K\( \alpha \), Co K\( \alpha \) and Ni K\( \alpha \) x-ray peaks are observed in the energy range 3-4 keV and a third order, \( n = 3 \), reflection for Fe K\( \alpha \) is also observed at \( \sim 2.1 \) keV.

Figure 3.51 WDX survey spectrum from a Kovar surface, collected over the energy range 0.2-8 keV.
3.5 X-ray photoelectron spectroscopy

3.5.1 Theory

The final technique used in this project was x-ray photoelectron spectroscopy (XPS), this enabled the elemental and chemical composition of the various sample surfaces to be monitored. In XPS a sample surface is exposed to x-rays of a known kinetic energy, as these x-rays collide with the atoms in the sample they cause the emission of inner shell electrons, as shown in Figure 3.52.

Upon the absorption of the x-ray photon, the excited atom can relax either by the emission of a photoelectron or by the Auger process. As each relies upon detecting the resulting electrons of similar energies, the depth of analysis of XPS is the same as for AES and was described in a previous section. The kinetic energy of the photoelectron is then analysed in the same way as previously described as for AES. However, unlike in AES, the convention for XPS is to plot the data on a binding energy scale. The kinetic energy of the photoelectron is then corrected to binding energy using the kinetic energy of the exciting photon. Typically aluminium or magnesium x-ray sources are used which generate Al Kα or Mg Kα x-rays with energies of 1486.6 and 1253.6 eV respectively.

The binding energies of the electron orbitals are different for each element and so the emitted electron can be used to characterise the elements present in the surface. As the energy of the electron orbital responds to changes in the chemical environment and because the energy resolution of XPS is so high it is not only possible to determine which elements are present but also their chemical state. The kinetic energy of the emitted electron is found using Equation 3.16 [64]:

\[ E_K = h\nu - E_B - W \] (3.16)

Where:

- \( E_K \) is the kinetic energy of the emitted electron (in eV), \( h\nu \) is the kinetic energy of the x-ray photon (in eV), \( E_B \) is the binding energy of the core electron (in eV) and \( W \) is the spectrometer work function (in eV).
The work function is the energy required for the electron to separate from its core hole and escape the surface from the Fermi level to the vacuum level. This value is typically \(~4\) eV.

### 3.5.2 Spectral interpretation

The appearance and features within a photoelectron spectrum depend upon the type of x-ray source that is used to excite the sample. This can be either an achromatic source, which typically uses aluminium and magnesium anode or a monochromated x-ray source, which typically uses an aluminium anode but can also be adapted for a silver anode. Figure 3.53 shows a survey spectrum collected from an aluminium metal surface using achromatic aluminium x-rays. The peaks present in the photoelectron spectrum can be divided into five categories, core transitions, valence transitions, Auger transitions, x-ray satellites and intrinsic loss peaks.

The binding energy of a photoelectron peak is characteristic of the element and the chemical environment of the atom. The transitions can: be single peaks in the case of the single degenerate electron orbitals like the 1s or doublets in the case of the doubly degenerate d orbitals split into the e_g and t_{2g} levels. The intensity of the two peaks within the doublet represents the ratio of the number of electrons that fill the degenerate energy levels. In some cases the energy levels of the degenerate orbitals are so close together that they cannot be clearly resolved in XPS. The width of the photoelectron peaks is a convolution of the natural line width, the line width of the exciting photoelectrons and the analyser resolution.

![Figure 3.53 Survey spectrum from an aluminium metal surface excited using an achromatic aluminium x-ray source.](image)

The exact binding energy of the peak provides chemical state information. The chemical shift is a change in peak energy (\(\Delta E\)) relative to the peak from a pure sample or a reference value. The shift is either positive or negative. This is because the electrons in an atom are either closer or further from the nucleus depending upon the type of electrostatic interaction between the bonding atoms. For example, the C 1s peak from the carbon atoms in polytetrafluoroethylene (PTFE), which is a particularly electronegative environment, will be located \(~292\) eV. This is considerably higher than standard binding energy of the aliphatic C 1s peak at 285 eV. For carbon in an electropositive environment, such as metallic carbide, the C 1s will be located at \(~283\) eV, lower than the standard binding energy.

The valence band represents the low binding energy electrons involved in bonding orbitals. They are found at \(>10\) eV, close analysis of the region can show the density of states within the material. It can also be useful...
for the identification of polymers when there is little difference in the C 1s peak structure, as is the case with polyethylene and polypropylene.

The Auger peaks are generated when the excited atom relaxes by the emission of an Auger electron instead of a photoelectron. They can provide a wealth of information if they are analysed correctly. One of the key pieces of information they can provide is chemical state information for elements which do not show noticeable shifts in the binding energy or the shape of the photoelectron peak. They can also enable the identification of chemicals states regardless of sample charging. This is achieved through the calculation of the modified Auger parameter ($\alpha^*$), as per Equation 3.17 [61]:

$$\alpha^* = E_{K \text{Auger}} + E_{\text{B photoelectron}} \quad (3.17)$$

Where:

$E_{K \text{Auger}}$ is the kinetic energy of the primary Auger transition and $E_{\text{B photoelectron}}$ is the binding energy of the photoelectron peak.

The Auger parameter is particularly useful in the analysis of copper compounds because metallic copper and copper (I) oxide show almost the exact same binding energy and peak shape. However, the Auger peaks are present at kinetic energies of 918.6 eV and 916.8 eV respectively. The difference in $\alpha^*$ is almost 2 eV for the copper compounds and because $\alpha^*$ represents the difference in the peak positions it will be the same even with sample charging. This provides a highly robust determination of the oxidation state of copper.

As well as the photoelectron and Auger peaks, x-ray satellites peaks are also present when the sample is analysed with an achromatic source. The satellite lines are the series of lower energy x-rays produced when the aluminium anode is excited and gives of an x-ray continuum. Figure 3.54 shows the energy levels involved in the generation of these x-rays.

![Figure 3.54 Schematic to show the energy levels involved in the generation of various x-ray satellite peaks in XPS.](image-url)
The Al Kα₁,₂ x-ray represents the majority of the x-ray intensity from the anode, the rest is made up of the Kβ, Kα₃,₄, Kα₅,₆ and background x-rays. A number of satellite peaks excited by the x-ray transitions are observed in the spectrum in Figure 3.53. The Kα₃,₄ satellites are observed ~10 eV below the O 1s and C 1s peaks and an O1s Kβ satellite is observed at ~465 eV. Table 3.8 shows the relative intensities of these x-ray lines.

### Table 3.8 X-ray satellite intensities from aluminium and magnesium x-ray sources

<table>
<thead>
<tr>
<th>Satellite peak separation and relative intensity</th>
<th>Magnesium anode</th>
<th>Aluminium anode</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray satellite Separation from Kα₁,₂ (eV)</td>
<td>Relative intensity (%)</td>
<td>Separation from Kα₁,₂ (eV)</td>
</tr>
<tr>
<td>Kα₃</td>
<td>8.4</td>
<td>9.2</td>
</tr>
<tr>
<td>Kα₄</td>
<td>10.0</td>
<td>5.1</td>
</tr>
<tr>
<td>Kα₅</td>
<td>17.3</td>
<td>0.8</td>
</tr>
<tr>
<td>Kα₆</td>
<td>20.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Kβ</td>
<td>48.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>

The photoelectrons that are generated within the interaction volume of the incident x-ray beam undergo both elastic and inelastic scattering within the solid. The elastically scattered electrons can escape from ~3λ. These form the photoelectron peaks as they retain all of the kinetic energy from the source photon minus the energy needed to overcome the binding energy of the electron.

Inelastic scattering can be extrinsic and intrinsic. The extrinsic loss generates the background (tail) after the photoelectron peaks they are produced by photoelectrons which, after being ejected from the host atom, lose some of their energy by inelastic scattering. The peak tails have characteristic gradients that can help in the interpretation of spectra. This is shown in Figure 3.55. (a) Shows the tail gradient behind a peak that was generated from atoms present at the extreme surface. The photoelectrons will have travelled the shortest distance to escape the surface, resulting in the fewest photoelectrons losing energy in inelastic collisions. (b) Shows photoelectrons that have had to travel a couple nanometres through the solid before escaping and so more have lost energy in the sample and end up at lower kinetic energies behind the photoelectron peak. (c) Shows electrons generated deep within the surface. A large proportion of the electrons generated from this depth will have lost energy from elastic collisions, resulting in a steep rising background following the photoelectron peak.

![Figure 3.55](image_url)
A steep rising background is characteristic of a material located deep in the surface and a falling tail is characteristic of a material at the extreme surface. A falling background is often seen at the higher binding energy side of the C 1s peak, on samples left in the atmosphere for a short time as the contamination is present at the sample surface. Intrinsic losses include: shake-up, shake-off and rare shake-down satellites. These satellites occur as the generated photoelectrons escaping the sample, interact with other electrons in the outer orbitals of other atoms.

Figure 3.56 shows three of the processes involved in these losses. (a) Shows the ejected photoelectrons kinetic energy losing a discrete amount of kinetic energy caused by exciting a valance electron into a higher energy valence orbital. A satellite peak is then observed at the higher binding energy side of the photoelectron peak. This is commonly observed in the form of a $\pi \rightarrow \pi^*$ shake-up transition after the C 1s peak in the analysis of polymers containing aromatic rings or delocalised electrons. (b) Shows the process for a shake-off peak. If the photoelectron causes a valence electron to be completely ejected from the atom, it loses a non-discreet amount of energy and contributes to the background at the lower kinetic energy side of the peak. (c) Shows the most uncommon, shake-down process. If the photoelectron gains a discrete amount of energy by the relaxation of a valence electron into a lower energy orbital, a shake-down peak will be observed at the higher kinetic energy of the photoelectron peak.

![Figure 3.56 Schematic of the three different intrinsic loss effects in XPS: (a) shake-up, (b) shake-off and (c) shake-down events.](image)

The background in spectrum that is produced from samples excited using an achromatic x-ray source consists of the inelastic electrons generated by the main aluminium x-rays as well as the Bremsstrahlung radiation. The Bremsstrahlung is the result of the continuum of x-rays that are produced by the source. These can have any energy up to the potential of the anode, which is typically 10-15 kV. These are generated within the source and are able to excite electrons within the sample. As the x-rays have a range of kinetic energies and undergo many inelastic collisions in the sample surface, the photoelectrons generated by them do not have discrete kinetic energies.

Through the use of an x-ray monochromator the ease with which a photoelectron spectrum can be interpreted can be improved. The monochromator has the effects of: removing the Bremsstrahlung background,
removing the x-ray satellites, reducing the x-ray line width (~0.8 eV to 0.3 eV), focusing the x-rays to a smaller spot size and it also reduces the signal intensity. The setup of a monochromator is shown in Figure 3.57. A bent and ground quartz crystal (10\(\overline{1}0\)) is placed on the surface of a Rowland sphere, (focusing circle) and the achromatic aluminium x-ray anode is placed at another point on the circle. The x-rays are dispersed by diffraction and refocused at another point on the sphere where the sample is placed.

The removal of x-rays other than the thin energy width of the K\(\alpha_{1,2}\) x-ray transition occurs as a result of destructive interference of the x-rays diffracted through the quartz crystal. For the first order, \(n = 1\) diffraction of Al K\(\alpha\), where \(\lambda = 0.83\) nm, the (10\(\overline{1}0\)) lattice spacing \(d = 0.425\) nm, the Bragg angle \(\theta = 78.5^\circ\), therefore the angle between incident and diffracted rays is 23\(^\circ\). If the sample is placed at this position in the Rowland sphere it will only be irradiated with the x-rays that have undergone constructive inference through the quartz crystal. These being the Al K\(\alpha_{1,2}\) x-rays of energy ~1486.6 eV.

![Figure 3.57 Schematic to show the setup of a monochromatic x-ray generation for XPS [80].](image)

Figure 3.58 shows a survey spectrum collected, using a monochromated aluminium x-ray source, from a beryllium surface following argon ion sputtering. The features present in the spectrum are largely the same as those in the survey collected using the aromatic x-ray source, although there are a few key differences. Firstly, the background intensity is considerably reduced as a consequence of removing the continuum of Bremsstrahlung x-rays. The intrinsic peak backgrounds are all similar showing a falling background behind the carbon and oxygen photoelectron and Auger peaks, indicating the carbon surface contamination and surface oxide. The background behind the beryllium photoelectron peak is more level showing it is located throughout the analysis depth. Secondly, the intensity of some of the weak impurity peaks has been reduced significantly, in particular fluorine, this is not a result of the argon sputtering as it is a bulk impurity, it is a consequence of the lower x-ray intensity of the monochromatic source. Thirdly, the x-ray satellites are no longer observed, there is no Al K\(\alpha_{3,4}\) peak to the low binding energy side of the O 1s and C 1s peaks and no O 1s K\(\beta\) peak, as these x-rays are removed by diffraction. The beryllium Auger transition is also present in the spectrum at ~1380 eV. This is not observed in the achromatic survey spectrum as the secondary electron tail dramatically increases the background and the Auger is lost in the noise.
Despite the benefits that the use of monochromatic x-ray sources provide, many modern XPS systems are also fitted with achromatic sources. These are for a variety of reasons including the ability to analyse samples for which using a flood gun for charge compensation proves problematic or for samples which outgas too much to utilise the flood gun. This occurs because the x-rays that are generated by the anode must pass through a thin sheet of aluminium foil in the nose of the gun. As they travel through the foil, they excite electrons that are able to compensate the surface for the ejected photoelectrons, providing a large degree of charge compensation. For rough samples, such as powders, where the use of depth profiling is impractical, the ability to change between magnesium and aluminium x-rays provides a small level of non-destructive depth profiling. The aluminium x-rays, being 233 eV higher in kinetic energy, are able to generate higher kinetic energy photoelectrons which can escape from ~1 nm deeper in the surface. They also allow for the use of Bremsstrahlung excited Auger transitions at higher kinetic energies, e.g. Si KLL and P KLL. These are at higher kinetic energies than can be excited by the aluminium or magnesium x-rays but can be excited by the high energy Bremsstrahlung x-rays.

However, their greatest advantage is highlighted in Figure 3.59 and Figure 3.60. These show the analysis of a Kovar glass-to-metal sealing alloy using achromatic aluminium and magnesium x-ray sources. Kovar is an alloy that consists of the transition metal elements: iron, nickel and cobalt. These elements all have intense Auger transitions that are in the vicinity of the main metal 2p peaks that are used for their analysis in XPS. While quantification and chemical information can be extracted from the less intense 3p or 3s transitions it is more desirable to use the 2p transition. By using a magnesium x-ray source the Auger transitions are shifted, on the binding energy scale, by the difference in kinetic energy of the aluminium and magnesium x-rays (~233 eV). This shift moves all of the Auger transitions out of the region of the metal 2p peaks, enabling their analysis without any interference from the previously overlapping Augers. A small Cr 2p peak is observed in the spectra as a result of slight x-ray spot overlap with another component.
Quantification in XPS is much simpler than in AES and should always be carried out as part of the sample analysis. The intensity of a photoelectron peak $I$, in a homogeneous sample, as per Equation 3.18:

$$I = J \rho \sigma K \lambda$$

(3.18)

Where:

$I$ is the peak intensity, $J$ is the photon flux, $\rho$ is the concentration of the atom or ion in the solid, $\sigma$ is the cross section for photoelectron production, $K$ is the spectrometer factor and $\lambda$ is the electron attenuation length. The cross-section for emission is the probability that a photoelectron will be emitted when the atom is irradiated with x-rays, it depends on the element, the electron orbital it is ejected from, and the energy of the exciting photon.

As the binding energy of an electron orbital becomes closer to the exciting photon energy, the cross section for photoelectron excitation increases. For example, the Mg 1s peak, at 1303 eV, is often observed to be
particularly large, even when magnesium is present at a low concentration for samples analysed using aluminium x-rays (1486.6 eV).

The spectrometer factor includes the transmission function, which is the proportion of electrons transmitted through the spectrometer as a function of the kinetic energy. The efficiency of the detector, which is the proportion of the electrons striking the detector that are actually detected. Stray magnetic fields can hinder the transmission of low energy electrons more than high energy electrons; this is also compensated for in the spectrometer factor. The intensity of a peak is usually taken as the integrated area under the peak following a Shirley background subtraction. The use of a linear background subtraction can result in a poor representation of the true peak area.

The instrument software uses experimentally or theoretically determined sensitivity factors such as Wagner or Scofield respectively to calculate the concentration of the elements in the solid [81,82]. These factors incorporate the terms: $\sigma$, $K$, and $\lambda$ from the peak intensity equation. If the x-ray flux is constant the concentration of an element A will be given by Equation 3.19:

$$[A\text{ at\%} = \frac{(I_A/F_A)/\Sigma(I/F)}{100} \quad (3.19)$$

Where:

I is the peak intensity, measured as the integrated area of the photoelectron peak after subtracting a suitable a background, and F is the sensitivity factor.

3.5.4 Experimental

Almost all elements in the periodic table can be analysed. There are fewer sample constraints in XPS analysis than there are for AES. So long as the sample is stable under UHV then XPS analysis can usually be performed. The analysis of insulating samples and polymers is routine in XPS unlike AES. Charge compensation is achieved through the use of flood gun which directs a beam of low energy electrons at the surface, with an argon gas bleed. In case of sample degradation under the x-ray beam, a shorter acquisition time can selected to minimise x-ray exposure.

XPS measurements were performed using a Thermo Scientific Theta Probe, shown in Figure 3.61. It is equipped with a twin anode (Al/Mg) and monochromatic Al source. The anode was typically operated at a power of 300 W and a 400 $\mu$m spot size. The electron take off angle was 53° relative to the sample normal and the transfer lens acceptance angle was 60°, centred on this position. For survey spectra a pass energy of 300 eV was used and for the high resolution spectra a lower pass energy of 30-80 eV was used. The aliphatic carbon C 1s peak was always set at a binding energy of 285.0 eV as reference to correct for any electrostatic charging.
3.5.5 XPS instrument analyser resolution

The FWHM of the Ag 3d$_{5/2}$ peak, at 368.16 eV, from a clean silver surface is usually used to assess the instrument analyser resolution. The ultimate instrumental analyser resolution is significantly smaller than this peak but because the FWHM of the Ag 3d$_{5/2}$ transition is 0.33 eV and is one of the narrowest photoelectron lines that can be readily acquired it provides a useful opportunity to study the change in resolution as a function of pass energy.

Initial survey spectra were collected on all samples investigated by XPS or AES as good practice. After survey spectra are collected using a high pass energy, high resolution spectra are collected with a much lower pass energy. The survey spectrum is always collected with a high pass energy to ensure that all elements within the sample, down to the detection limit of ~0.1 at.%, can be observed within the spectrum. The high pass energy gives a huge increase in signal intensity, at the cost of energy resolution, over the lower pass energies. This is shown in Table 3.9.

Table 3.9 Relationship between pass energy and signal intensity of the Theta Probe spectrometer

<table>
<thead>
<tr>
<th>Pass energy (eV)</th>
<th>FWHM of Ag 3d$_{5/2}$ (eV)</th>
<th>Relative intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>2.12</td>
<td>534.4</td>
</tr>
<tr>
<td>200</td>
<td>1.52</td>
<td>374.6</td>
</tr>
<tr>
<td>100</td>
<td>0.90</td>
<td>163.8</td>
</tr>
<tr>
<td>90</td>
<td>0.85</td>
<td>143.4</td>
</tr>
<tr>
<td>80</td>
<td>0.79</td>
<td>120.9</td>
</tr>
<tr>
<td>70</td>
<td>0.74</td>
<td>98.7</td>
</tr>
<tr>
<td>60</td>
<td>0.69</td>
<td>77.8</td>
</tr>
<tr>
<td>50</td>
<td>0.65</td>
<td>55.8</td>
</tr>
<tr>
<td>40</td>
<td>0.60</td>
<td>38.5</td>
</tr>
<tr>
<td>30</td>
<td>0.56</td>
<td>23.3</td>
</tr>
<tr>
<td>20</td>
<td>0.54</td>
<td>11.1</td>
</tr>
<tr>
<td>10</td>
<td>0.51</td>
<td>3.1</td>
</tr>
<tr>
<td>5</td>
<td>0.50</td>
<td>1</td>
</tr>
</tbody>
</table>


3.5.6 XPS instrument calibration

It is important that the user of an instrument has the highest confidence in the quality of the data produced. While more modern XPS instruments are able to self-calibrate the energy scale, the Theta Probe requires the user to check that the spectrometer itself is operating normally. This includes a simple procedure to analyse pure samples of gold, silver and copper and record the binding energies of their primary photoelectron peaks. These are routinely used as reference materials in XPS as they are commonly available and are well characterised. It is desirable to use all three metals as each has an intense peak at different regions of the energy scale. If gold and silver are not available then a clean, oxide free sample of copper can be used in their place as copper has peaks throughout the energy range: Cu 3p, Cu LMM, and Cu 2p.

Gold has a low binding energy peak Au 4f$_{7/2}$, silver a mid-range binding energy peak Ag 3d$_{5/2}$ and copper a high binding energy peak Cu 2p$_{3/2}$. By encompassing the full energy range it is possible to look for shifts at high or low binding energies or for stretch within the spectrum. Each of these suggests that the voltages on the hemispheres of the analyser are incorrect. The reference values supplied by the National Physical Laboratory and the National Institute of Standards and Technology are shown in Table 3.10 [83].

<table>
<thead>
<tr>
<th>Transition</th>
<th>Binding energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au 4f$_{7/2}$</td>
<td>83.95</td>
</tr>
<tr>
<td>Ag 3d$_{5/2}$</td>
<td>368.21</td>
</tr>
<tr>
<td>Cu 2p$_{3/2}$</td>
<td>932.62</td>
</tr>
<tr>
<td>Cu L$<em>{3}$M$</em>{4,5}$</td>
<td>567.93</td>
</tr>
<tr>
<td>Cu 3p$_{3/2}$</td>
<td>75.14</td>
</tr>
</tbody>
</table>

High resolution spectra were collected from pure gold, silver and copper samples following a brief argon ion etch to remove surface contamination and oxide. A step size of 0.01 eV, pass energy of 5 eV and 100 total scans were used to ensure the most accurate peak position. The binding energies of the three metals are shown in Table 3.11. The binding energy of the three transitions was found to be correct to within 0.1 eV. As the majority of XPS data collected within the laboratory is recorded with a step size of 0.1 eV, changes to the instruments hemisphere voltages were not deemed to be necessary.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Binding energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au 4f$_{7/2}$</td>
<td>83.85</td>
</tr>
<tr>
<td>Ag 3d$_{5/2}$</td>
<td>368.16</td>
</tr>
<tr>
<td>Cu 2p$_{3/2}$</td>
<td>932.61</td>
</tr>
<tr>
<td>Cu L$<em>{3}$M$</em>{4,5}$</td>
<td>567.94</td>
</tr>
</tbody>
</table>

In addition to collecting the binding energies of the three metals that provide information about the performance of the analyser, it is also wise to acquire the principle Cu L$_{3}$M$_{4,5}$ Auger transition at the same time. Measurement of the Auger peak positions provides a good indication of the alignment of the x-ray monochromator crystal. If the peak position is more than ±0.2 eV from the reference value, 1486.61 eV, then the quartz crystal needs to be realigned. The x-ray photon should have an energy of 1486.61 - 1486.81 eV. The difference of 0.01 eV in the reference and recorded values shows that the Theta Probe monochromator is setup correctly and taking the middle, most intense, part of the Al Kα$_{1,2}$ x-ray transition.
3.6 Conclusions

The majority of the work described in the following chapters was performed using AES and EDX, although XPS and WDX were employed on a number of occasions. An overview of these techniques has been given in this chapter together with the important theory related to the investigative techniques and examples of their use.

In the next chapter the corrosion of an aluminium alloy AA7075-T6 will be described. This investigation required the use of multiple characterisation techniques and presented a useful learning opportunity to develop proficiency in the instruments and the theory required for this project, prior to the investigation of beryllium with the appropriate health and safety requirements.
Chapter 4 - Corrosion of a 7075-T6 Aluminium alloy

4.1 Introduction
To develop the methodology to investigate the corrosion of beryllium, a non-toxic metal analogue was chosen. This would enable the material to be safely used during the optimisation of the instrumental and corrosion processes, without the risk of exposure of myself or co-workers to a hazardous material. Aluminium AA7075-T6 was chosen as a suitable precursor metal.

Aluminium and aluminium alloys are well-studied materials which undergo pitting corrosion in chloride containing solutions at similar concentrations as has been used for beryllium [84]. The aluminium alloy 7075-T6 was chosen for this investigation. This was selected as the pitting corrosion processes associated with this alloy had not previously been investigated using the experimental methodology in this thesis and an alloy sample was readily available from a previous project. More importantly, the second phase particles present in the alloy were known to have a range of compositions and be of a similar size as those known to occur in beryllium, 0.1-30 µm.

4.2 AA 7075-T6 Literature review
AA7075 is widely used within the aerospace industry because of the high specific strength to weight ratio of the alloy. The 7xxx series (Al-Zn-Mg-Cu alloys) provide the potential for precipitation hardening throughout a range of compositions. However, they can suffer from poor corrosion resistance, resulting from localised corrosion (pitting).

The thin passive oxide on aluminium is protective as it is highly insulating, preventing reactions at the metal surface. Therefore, aluminium is more prone to experience localised corrosion at the site of second phase constituent particles which interfere with the homogeneity of the oxide. Heterogeneities at the surface of aluminium alloys include grain boundaries and second phase particles. At these sites defects in the oxide film are believed to exist. There can also be galvanic activity between the particles and the matrix. The defects and active particles, are responsible for the formation of pits when aluminium alloys are exposed to aqueous corrosive media [85,86].

Extensive investigation into the surface layer has shown that the first corrosive breakdown of mechanically polished AA7075 is associated with a rapid dissolution of a thin surface layer ~100 nm thick. The layer formation is the result of the damage caused by mechanical polishing. The high compressive and shear stresses at the surface results in a significant decrease in the number of fine precipitates and causes large intermetallics to break up. Additionally, the magnesium and zinc from the fine precipitates enter solid solution and form a solute rich zone resulting in the initial anodic attack of this thin surface layer [87].

AA7075 alloy has a nominal composition of Si 0.4, Fe 0.5, Cu 1.2-2.0, Mn 0.3, Mg 2.1-2.9, Zn 5.1-6.1, Cr 0.18-0.28, Ti 0.2 wt.% and Al remainder, with trace amounts of other elements [88]. Alloying elements present in aluminium are either in solid solution or segregated as second phase micro-constituents. The
composition of these secondary phases can range from a single element such as silicon, a compound of two elements such as MgZn$_2$ or as a compound containing aluminium together with one or more alloying elements, such as Al$_2$CuMg.

These particles fall into one of three categories: hardening precipitates, dispersoids and constituent particles. Hardening precipitates range in size up to ten nanometres, MgZn$_2$ is a common example [89]. Dispersoids help to control grain size and can grow to hundreds of nanometres. These include Al$_3$Ti, Al$_6$Mn and Al$_3$Zr. Constituent particles are the largest second phase particles and can grow to tens of micrometres. They are formed during solidification and more than a dozen types are known to occur in AA 7075 [85]. Typical compositions include; Mg$_2$Si, MgZn$_2$ (η phase), Al$_2$CuMg (S phase), (Al,Cu)$_6$(Fe,Cu), Al$_3$Cu$_2$Fe and Al$_3$Fe [88]. The most numerous of these have been identified as (Al,Cu)$_6$(Fe,Cu) and Al$_3$Cu$_2$Fe [90]. From the large potential differences, the intermetallics concentrated in copper are known to act as cathodes to the aluminium alloy, resulting in the active dissolution of the surrounding alloy matrix upon exposure to a corrosive solution.

Magnesium and zinc are anodic with respect to the bulk alloy. Therefore, intermetallics concentrated in these are likely to dissolve preferentially to the matrix. It has been observed that magnesium rich intermetallics, such as Mg$_2$Si, can be anodic or cathodic to the matrix depending upon the type of heat treatment performed on the alloy [91]. This occurs as a result of the dissolution or formation of MgZn$_2$ particles in the alloy. Their dissolution increases the magnesium and zinc concentrations within the alloy making it more anodic, which can drive the Mg$_2$Si particles to be cathodic to the matrix [92]. Whether the various intermetallics are anodic or cathodic to the matrix the result is the same, a pit is formed either by the dissolution of the intermetallics or by their undermining and eventual release from the surface as the surrounding matrix is dissolved.

The primary corrosion in aluminium alloys is localised, pitting, corrosion, associated with second phase particles which are usually 0.1-30 µm in diameter. Therefore, techniques with high spatial resolution are required to study the microchemistry of individual intermetallics. For the study of pitting corrosion and the microchemistry of individual particles, a combination of surface specific SEM, AES and SAM techniques, in addition to a bulk analysis technique, EDX, has been shown to provide a great deal of understanding in multiple metal systems [54,56,57,93].

### 4.3 Experimental

A 1 cm$^2$ sample of AA7075 was wet ground with 600, 1200, 2500 and 4000 grit silicon carbide papers and then polished to a 1 µm finish. It was then ultrasonically cleaned using acetone and rinsed in DDI water. The cleaned and polished metal sample was wrapped in aluminium foil and stored in a vacuum desiccator between analyses.

Ten secondary phase particles were identified using RLM in different stringers of second phase particles, aligned perpendicular to the rolling direction of the alloy. A 200 g Vickers microhardness indent was placed at the edge of the sample and at the start of the area containing the ten intermetallics. This enabled easier,
subsequent location of the intermetallics. In addition to this, each intermetallic was marked using three smaller 20 g microhardness indents. Each indent was located at least 50 µm from the intermetallics. EDX was performed on each of the intermetallics and their compositions determined from the resultant spectra. From the EDX analysis, three were chosen for further investigation. These three had an increasing concentration of copper and varying morphology.

A 3.5 wt.% (0.47 M), pH 7 solution of potassium chloride was prepared from analytical grade KCl and DDI water. The specimen was analysed in the as-cleaned and polished state and then the specimen was immersed, analysis side up, into the KCl solution for cumulative time periods of 15, 45 min, 2, 4, 8 and 16 hours. The same three intermetallics were repeatedly located and positioned such that the FOV in the SEM was as close to constant as possible for each immersion time.

Following immersion, the specimen was rinsed with DDI to remove the remaining KCl solution. The excess water was then drained onto lint free tissue. The sample was then loaded into the entry lock of the spectrometer which was evacuated until UHV was achieved and the sample could be transferred to the analysis chamber of the spectrometer. The sample was then imaged using an SEM and analysis performed by AES, SAM and EDX. The surface sensitive techniques AES and SAM were performed prior to EDX, to minimise the build-up of carbon contamination on and around the intermetallics during analysis.

The investigation was performed using a Thermo Scientific MICROLAB 350 scanning Auger microscope fitted with an integral Thermo Scientific EDX detector. This configuration enables the acquisition of SAM and EDX maps from the same region of the surface, without the need to reposition, relocate or remove the sample from vacuum. A primary electron beam energy of 10 keV was used for the acquisition of point Auger spectra and a beam energy of 15 keV was used for the acquisition of EDX spectra and SAM maps. These settings provided beam currents of ~4 nA and 8 nA respectively. A gun aperture of 50 µm was used providing a spatial resolution of ~40 nm in AES.

Auger survey spectra were recorded with an energy range of 20-1800 eV and a retard ratio of 4. SAM maps were recorded with a retard ratio of 2.8, to increase sensitivity. 128² pixel SAM maps and 285² pixel EDX maps were acquired, for all of the elements present in the intermetallics, with acquisition times of approximately 17 hours and 8 hours respectively.

To remove the carbon contamination deposited onto the surface by polishing, the sample was lightly argon ion etched. This was performed using a beam energy of 1 keV and sample current density of 0.05 µA cm⁻². Sputtering was not repeated during the investigation to ensure no corrosion products or aggressive ions at the surface were removed. After 16 hours of immersion and following the final AES, SAM and EDX analysis, each of the three intermetallics was cross sectioned using focused ion beam (FIB) milling. Milling was performed using a FEI nano-Nova dual-beam FIB microscope with a beam current of <3 nA and an accelerating voltage of 20 kV. Following the complete immersion experiment and after FIB milling the intermetallics were imaged using a JEOL JSM 7100-F SEM at a beam energy of 15 keV.
Topographic effects in the SAM maps were minimised by displaying the images as a result of the algorithm \((P-B)/(P+B)\), where: \(P\) is the intensity of the Auger peak and \(B\) is the intensity of the background. A Thermo Scientific Avantage V4.87 data system was used for the acquisition and processing of the Auger data and Thermo Scientific Noran System Seven was used for the acquisition and processing of the x-ray data and generation of the x-ray phase maps.

4.4 Results

4.4.1 General results and observations

The freshly polished sample of AA7075 was examined using RLM and SEM. This showed the presence of numerous second phase particles with sizes from 0.1 to 30 \(\mu\)m. The intermetallics were aligned in stringers with the working direction of the alloy, as shown in Figure 4.1. The large microhardness indent on the left side of the image was produced using a 200 g load for ten seconds and was used to easily locate the region of interest in the SEM. The intermetallics were marked along a single movement in the x-axis, working outwards from the large indent. This accelerated subsequent locating of the marked intermetallics. The ten marked intermetallics were initially selected from the numerous surrounding intermetallics, as their sizes were all similar, \(~3-5\) \(\mu\)m. This size range was desired as they are directly comparable to the size of intermetallics encountered in beryllium S-65, which is examined in Chapter 6 [23].

![Figure 4.1 Low magnification RLM image of the aluminium alloy surface with the ten marked intermetallics numbered.](image)

It was attempted to keep the microhardness indents at least 50 \(\mu\)m away from the intermetallic of interest to try and minimise any effects of residual strain in the local aluminium which could have an effect on the corrosion process. Figure 4.2 shows a higher magnification RLM image of the arrangement of the microhardness indents around an intermetallic. The indents form three corners of a square with the fourth made up by the intermetallic.
Using ImageJ software, the SEM micrographs of the intermetallics were analysed and their total area calculated [94]. These are shown in Table 4.1. The mean intermetallic area was 20.4 µm². Although the intermetallics were numbered 1-10, only three were chosen for further analysis. The final column in the table shows the numbers of the intermetallics as they are presented in this chapter. While it was attempted to ensure the intermetallics were of similar size, there was some variation and the third intermetallic was >50% larger than the first two.

### Table 4.1 Area of the ten intermetallics previously marked

<table>
<thead>
<tr>
<th>Intermetallic number as marked</th>
<th>Intermetallic area (µm²)</th>
<th>Intermetallic number used in this chapter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>19.5</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>5.5</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>27.2</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>7.3</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>16.9</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>23.2</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>30.2</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>5.1</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>15.2</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>22.5</td>
<td>-</td>
</tr>
<tr>
<td><strong>Mean</strong></td>
<td><strong>20.3</strong></td>
<td><strong>-</strong></td>
</tr>
</tbody>
</table>

After marking each of the intermetallics with microhardness indentations, each was analysed using EDX. Additionally, an EDX spectrum was acquired from a 25 mm² area to determine the average bulk composition of the alloy. The EDX spectrum collected from the alloy is shown in Figure 4.3. The spectrum shows intense Al Kα, Mg Kα and Zn Lα x-ray peaks together with weaker C Kα, O Kα and Cu Kα peaks. The carbon and oxygen peaks are present as a result of x-rays emitted from surface hydrocarbon contamination and the oxide layer respectively. A weak aluminium sum peak is also observed at ~3 keV.
Figure 4.3 EDX spectrum collected from the bulk aluminium alloy. Al+Al is the aluminium sum peak.

Quantification was performed on the EDX data collected from the ten intermetallics. This is shown, together with the average composition of the ten and the bulk alloy composition, in Table 4.2. The intermetallics are rich in aluminium and elements that exhibit low solubility in aluminium, typically iron, silicon and copper. Following quantification, three intermetallics were chosen for further analysis, these are highlighted in the table and the numbers by which they are identified throughout the rest of this chapter are shown in brackets. After selecting the three intermetallics the sample was moved to the MICROLAB 350 to continue the investigation.

Table 4.2 Compositions of ten marked intermetallics in addition to the bulk composition, the numbers in brackets are the designations for intermetallics in this chapter

<table>
<thead>
<tr>
<th>Intermetallic</th>
<th>Al</th>
<th>Mg</th>
<th>Si</th>
<th>Cr</th>
<th>Fe</th>
<th>Cu</th>
<th>Zn</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (2)</td>
<td>76.7</td>
<td>0.7</td>
<td>0.3</td>
<td>3.4</td>
<td>11.3</td>
<td>4.9</td>
<td>2.4</td>
<td>0.3</td>
</tr>
<tr>
<td>2</td>
<td>79.0</td>
<td>0.6</td>
<td>4.7</td>
<td>2.9</td>
<td>10.3</td>
<td>1.3</td>
<td>1.2</td>
<td>ND</td>
</tr>
<tr>
<td>3 (3)</td>
<td>71.1</td>
<td>0.3</td>
<td>ND</td>
<td>ND</td>
<td>8.0</td>
<td>18.3</td>
<td>1.7</td>
<td>0.9</td>
</tr>
<tr>
<td>4</td>
<td>84.5</td>
<td>1.9</td>
<td>2.7</td>
<td>0.6</td>
<td>6.7</td>
<td>1.2</td>
<td>2.4</td>
<td>ND</td>
</tr>
<tr>
<td>5 (1)</td>
<td>72.5</td>
<td>ND</td>
<td>5.1</td>
<td>3.7</td>
<td>16.7</td>
<td>1.6</td>
<td>0.4</td>
<td>ND</td>
</tr>
<tr>
<td>6</td>
<td>75.6</td>
<td>ND</td>
<td>6.1</td>
<td>3.4</td>
<td>12.3</td>
<td>1.6</td>
<td>1.0</td>
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<tr>
<td>7</td>
<td>78.0</td>
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<td>0.2</td>
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<tr>
<td>8</td>
<td>88.2</td>
<td>2.4</td>
<td>1.6</td>
<td>0.3</td>
<td>4.0</td>
<td>1.0</td>
<td>2.5</td>
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</tr>
<tr>
<td>9</td>
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<td>3.8</td>
<td>1.6</td>
<td>5.9</td>
<td>1.2</td>
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<td>ND</td>
</tr>
<tr>
<td>10</td>
<td>79.3</td>
<td>1.3</td>
<td>1.3</td>
<td>2.4</td>
<td>8.0</td>
<td>4.8</td>
<td>2.5</td>
<td>0.4</td>
</tr>
<tr>
<td>Intermetallic at.% avg</td>
<td>80.1</td>
<td>1.4</td>
<td>3.0</td>
<td>1.8</td>
<td>8.3</td>
<td>3.3</td>
<td>1.8</td>
<td>0.4</td>
</tr>
<tr>
<td>Intermetallic wt.% avg</td>
<td>67.3</td>
<td>1.1</td>
<td>2.7</td>
<td>3.0</td>
<td>14.6</td>
<td>6.7</td>
<td>3.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Bulk wt.%</td>
<td>90.2</td>
<td>2.6</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>1.4</td>
<td>5.5</td>
<td>ND</td>
</tr>
<tr>
<td>Bulk at.%</td>
<td>93.6</td>
<td>3.0</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.7</td>
<td>2.4</td>
<td>ND</td>
</tr>
</tbody>
</table>

After moving the sample into the spectrometer, the surface was lightly argon ion sputtered prior to acquisition of the first AES and SAM maps. This was performed to remove the thin carbonaceous contamination left on the surface by polishing. The thickness of this carbon layer was likely to have further built-up over the course of the experiment and attenuate the Auger electrons from the substrate required for elemental analysis. Figure 4.4 shows the AES survey spectra collected from each of the three intermetallics. The Al KLL Auger transition was observed in each of the spectra and both the aluminium oxide and metal peaks were present. The kinetic energies of the most intense $KL_2,3L_2,3$ peaks were 1386.5 eV and 1393.0 eV.
respectively. Broad Al LMM transitions are also present at ~68 eV for each of the intermetallics. Weak Fe LMM peaks are observed in all of the spectra and the $L_3M_{4,5}M_{4,5}$ peak was centred at 702.5 eV. An intense O KLL peak was observed in the spectra from the first and second intermetallics with a weaker peak observed on the third intermetallic. In each case the $KL_{2,3}L_{2,3}$ peak was located at 506.5 eV. The differences in intensities between the first two and the third intermetallic indicated that a thinner oxide was present on the third intermetallic. While the first intermetallic does not show any copper Auger transitions, the second and third intermetallics show weak and intense Cu LMM peaks respectively. The position of the most intense $L_3M_{4,5}M_{4,5}$ peak was measured as 917.5 eV, which is suggestive of CuO. The first intermetallic showed a weak Si KLL Auger transition at ~1618 eV and a weak Si LMM Auger transition at ~90 eV. These peaks were too weak to locate a true peak position in order to determine the chemical state of silicon. A weak C KLL peak was observed on each of the intermetallics at 270.5 eV, as a consequence of a thin remaining contamination layer.

![Figure 4.4 AES survey spectra collected from each of the three intermetallics after light argon ion etching to remove the contamination layer. The number next to each spectrum shows the intermetallic is was acquired from.](image)

### 4.4.2 Intermetallic #1

#### 4.4.2.1 Initial analysis of the first intermetallic

Following the acquisition of the initial AES survey spectrum, the intermetallic was imaged using the SEM. Figure 4.5 (a) shows the SEM micrograph of Intermetallic #1. The dimensions of the intermetallic were ~4 x 3 μm². The two points identified in yellow, Point 1 in the centre of the intermetallic and Point 2 on the nearby matrix show the positions that were chosen for AES and EDX point analysis. The EDX spectra collected from Points 1 and 2 as well as the EDX phase maps of the region are shown in Figure 4.6. Based upon the composition obtained from EDX quantification, the intermetallic was believed to be Al$_{12}$Fe$_3$Si.
Figure 4.5 SEM micrographs of Intermetallic #1, (a) before immersion and (b) after 16 hours of immersion in KCl. Points 1 and 2 refer to the positions from which AES and EDX point spectra were collected.

Figure 4.6 (a) shows the EDX spectra collected from Points 1 and 2 on the intermetallic and the matrix. The spectrum from Point 2 matches that of the matrix surrounding the other intermetallics and the bulk alloy. The spectrum from Intermetallic #1 shows an intense Al Kα peak together with weaker Fe Kα, Si Kα and Cr Kα peaks. A particularly weak Cu Kα peak was also observed. Figure 4.6 (b + c) shows the phase maps generated from EDX count maps of the intermetallic. They showed that within the analysis depth of the primary electron beam, which was a maximum of 1.5 µm at 15 keV, the intermetallic was homogeneous in composition. They also showed that the point analysis performed on the centre of the intermetallic accurately represents the entire composition. In addition to the primary intermetallic, two smaller intermetallics are also observed within the analysed area. These smaller intermetallics have the same or a very similar composition as the main intermetallic as they show up as the same phase during phase mapping.
Quantification of the EDX spectra collected from Intermetallic #1 and the surrounding matrix is shown in Table 4.3. The intermetallic was concentrated in iron, containing considerably more than Intermetallics #2 and #3. Small amounts of chromium, silicon and copper are also present. The matrix quantification was consistent with values expected for AA7075 and the values obtained in Table 4.2.

![Figure 4.6](image)

**Table 4.3** EDX quantification of Intermetallic #1 and the adjacent matrix (normalised)

<table>
<thead>
<tr>
<th>Region/Composition</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>Cr</th>
<th>Fe</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intermetallic (wt.%)</td>
<td>ND</td>
<td>58.3</td>
<td>3.3</td>
<td>5.9</td>
<td>27.9</td>
<td>3.1</td>
<td>1.5</td>
</tr>
<tr>
<td>Matrix (wt.%)</td>
<td>1.9</td>
<td>88.6</td>
<td>ND</td>
<td>0.2</td>
<td>ND</td>
<td>1.9</td>
<td>7.4</td>
</tr>
<tr>
<td>Intermetallic (at.%)</td>
<td>ND</td>
<td>72.5</td>
<td>5.1</td>
<td>3.7</td>
<td>16.7</td>
<td>1.6</td>
<td>0.4</td>
</tr>
<tr>
<td>Matrix (at.%)</td>
<td>1.8</td>
<td>94.9</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>0.8</td>
<td>2.5</td>
</tr>
</tbody>
</table>

### 4.4.2.2 AES and SAM results as a function of time

The SEM micrographs and the elemental SAM maps generated from Intermetallic #1 were arranged into rows as a function of immersion time, as shown in Figure 4.7. This enables the morphological and compositional changes brought about by the corrosion processes to be more easily observed. Examination of the SEM micrographs showed little change to the intermetallic throughout the immersion time. There were no apparent corrosion products on the surface of the intermetallic and no accelerated corrosion of the surrounding matrix was observed. Examination of the SAM maps reveal that after 15 minutes of immersion the transition metal peaks become significantly less intense and their presence was no longer observed in the maps after 45 minutes. The slight observed trace of chromium was possibly a result of the Cr LMM region overlapping with the O KLL transition and having an effect on the mapped energy. The most significant
change occurred after 8 hours of immersion. The region of low signal intensity in the aluminium and oxygen maps becomes more delocalised, with the reduced intensity appearing to move out from the intermetallic and onto the adjacent matrix.

This was likely to have been caused by the increased surface roughness as the matrix undergoes general corrosion. This will act to decrease the signal intensity and increase the background in the spectrum. A halo of low signal intensity was observed at the interface between the intermetallic and the matrix after 8 hours which is more noticeable after 16 hours. The elemental maps in addition to the SEM micrographs indicated the formation of a crevice at the interface. No evidence was observed for the dissolution of the intermetallic.

Figure 4.7 SEM micrographs (first row) and the SAM maps of Al, O, Fe, Cr and Si at different immersion times for Intermetallic #1.

AES survey spectra collected from Point 1 at the centre of Intermetallic #1 after 45 minutes, 4 hours and 16 hours are shown in Figure 4.8. They show, more clearly than the SAM maps, how the surface changes over the course of the investigation. While the point spectra provide more information than the maps they only represent the single pixel they were collected from.

From the point spectra it can be seen that the surface of the intermetallic changed little during the 16 hour immersion time. After 45 minutes the spectrum still appeared to be very similar to the spectrum shown in Figure 4.4 at time zero. The Fe LMM, Si KLL, Al KLL and O KLL Auger transitions are all still clearly observed, although there was a slight increase in intensity of the C KLL.
After 4 hours and further to 16 hours of immersion, the intensity of the Fe LMM peaks falls compared to the intensity observed in the spectrum that was collected after 45 minutes of immersion. The ratio of the Fe LMM to the Al KLL and O KLL peaks also decreases. This could be caused by either a slight increase in the thickness of aluminium oxide/hydroxide, partial dissolution of the iron at the surface of the intermetallic or possibly the slight deposition of aluminium hydroxide corrosion products on the surface. The trend in the point spectra fit well with that observed in the iron SAM maps, as the Fe LMM intensity on the intermetallic appeared to decrease significantly between 45 minutes and 2 hours of immersion.

![AES survey spectra from Intermetallic #1 after 45 min, 4 hours and 16 hours. Each was collected from Point 1 as shown in Figure 4.5.](image)

**Figure 4.8 AES survey spectra from Intermetallic #1 after 45 min, 4 hours and 16 hours. Each was collected from Point 1 as shown in Figure 4.5.**

### 4.4.2.3 EDX results as a function of time

The SEM micrographs, in addition to the elemental EDX maps, from Intermetallic #1, are shown in Figure 4.9. The maps show that the size and shape of the intermetallic in the transition metal maps and in the aluminium and magnesium maps does not change throughout the investigation. This showed that the bulk of the intermetallic had not been corroded. It was observed that the surrounding matrix did undergo some corrosive attack. Between 4 hours and 8 hours of immersion, the surface of the matrix became significantly rougher and small pits were observed. These were probably associated with the dissolution of anodic MgZn\(_2\) precipitation hardening particles that were too small to reliably detect with EDX. As the surface roughness increases EDX becomes increasingly sensitive to low energy x-rays. This caused the apparent concentration of oxygen to increase resulting in bright regions in the oxygen EDX map on the surrounding matrix. The dark halo at the matrix-intermetallic interface that was observed in the oxygen SAM map was considerably more pronounced in the 16 hour oxygen EDX map. The halo completely surrounded the intermetallic, indicating significant crevice formation at the interface. Some of the reduction in intensity can be associated with the position of the EDX detector in the spectrometer and shadowing of the surface by the topography on the intermetallic. This causes regions on the right hand side of the image to be in shadow if a high region of material is to the left.

A number of additional smaller intermetallics are detected by EDX within the field of view (FOV). Two of these are observed in the EDX phase map in Figure 4.6 (b + c) and not observed in the SAM maps. The first small intermetallic was located in the upper left corner of the FOV and was most noticeable in the iron map.
Below this there was also another slightly larger intermetallic at the edge of the FOV, which is most noticeable in the 2 hour maps as the SEM FOV is aligned further to the left during this analysis run. A third smaller intermetallic was observed beneath the primary intermetallic in the iron EDX maps. The final intermetallic was observed in all of the magnesium EDX maps and is located in the bottom mid/left of the FOV. It appeared to be entirely subsurface, as it was not observed in any of the SEM micrographs.

![SEM micrographs and EDX maps](image)

**Figure 4.9** SEM micrographs (first row) and the EDX maps of Al, O, Fe, Cu, Cr, Zn and Si and Mg at different immersion times for Intermetallic #1.

### 4.4.2.4 FIB cross sectioning

Following the investigation by AES and EDX the intermetallic was cross sectioned using FIB milling. Figure 4.10 shows the SEM micrographs collected following milling. They show how the interface between the intermetallic and the matrix had been severely corroded while the matrix surface surrounding the
intermetallic did not appear to have been adversely affected by the presence of the intermetallic. The surrounding matrix surface is fairly flat and remains parallel to the surface of the intermetallic. Additionally, the surface of Intermetallic #1 remained in the smooth as-polished state, with no evidence for the deposition of corrosion products.

![Figure 4.10 SEM micrographs of Intermetallic #1 after FIB milling: (a) whole of the intermetallic and (b) higher magnification view of the crevice.](image)

4.4.3 Intermetallic #2

4.4.3.1 Initial analysis of the second intermetallic

The experimental steps that were performed for Intermetallic #1 were repeated for Intermetallic #2. Figure 4.11 (a) shows the SEM micrograph of Intermetallic #2 prior to immersion. It was ~4 x 2 μm² in size and rectangular in shape. Points for AES and EDX analysis where chosen in the centre of the intermetallic Point 1 and on the matrix Point 2. The EDX spectra from the points 1 and 2 are shown in Figure 13. From the EDX quantification of Intermetallic #2, it is believed to be an Al₇Fe₂Cu intermetallic.

![Figure 4.11 SEM micrographs collected from the Intermetallic #2. (a) before immersion and (b) after 16 hours immersion in KCl solution. Points 1 and 2 refer to the positions from which AES and EDX point analyses were collected.](image)

Figure 4.12 (a) shows the EDX spectra collected from the intermetallic, Point 1, and the matrix, Point 2, in Figure 4.11. The spectrum from the nearby matrix matches those for the bulk alloy and the matrix surrounding Intermetallic #1. The spectrum from the intermetallic shows an intense Al Kα peak together with
Weaker Fe Kα, Cu Kα and Cr Kα peaks. In addition to these there are weaker Si Kα, Mg Kα and Zn Kα peaks. Figure 13 (b + c) show the phase maps produced from the elemental EDX count maps. They showed that within the analysis depth of the electron beam the intermetallic was homogeneous in composition. This was also true for the surrounding matrix. They also showed that the quantification performed on the point EDX spectra accurately represented the intermetallic composition.

![Figure 4.12](image)

Figure 4.12 (a) EDX spectra collected from Intermetallic #2 and the matrix. (b + c) EDX phase maps of the matrix and intermetallic respectively.

Quantification of the EDX spectra collected from Intermetallic #2 and the matrix is shown in Table 4.4. It has been normalised to 100 wt.% after omitting oxygen and carbon. These are omitted as they are not part of the alloy and are only present as surface oxide and contamination respectively. As the x-rays are of very low energy, <1 keV, their removal from the quantification was unlikely to have had a significant effect on the overall concentrations of other elements. The intermetallic was concentrated in elements that are poorly soluble in aluminium. Iron and copper were present at the highest concentrations together with small amounts of chromium and traces of nickel and silicon.

<table>
<thead>
<tr>
<th>Region/Composition</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>Cr</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intermetallic (wt.%)</td>
<td>0.5</td>
<td>61.0</td>
<td>0.3</td>
<td>5.2</td>
<td>18.7</td>
<td>0.6</td>
<td>9.2</td>
<td>4.6</td>
</tr>
<tr>
<td>Matrix (wt.%)</td>
<td>1.7</td>
<td>89.0</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>0.8</td>
<td>7.5</td>
</tr>
<tr>
<td>Intermetallic (at.%)</td>
<td>0.7</td>
<td>76.7</td>
<td>0.3</td>
<td>3.4</td>
<td>11.3</td>
<td>0.3</td>
<td>4.9</td>
<td>2.4</td>
</tr>
<tr>
<td>Matrix (at.%)</td>
<td>2.0</td>
<td>93.9</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>0.8</td>
<td>3.3</td>
</tr>
</tbody>
</table>

4.4.3.2 AES and SAM results as a function of time

In the same manner as the first intermetallic the SEM micrographs and the elemental SAM maps were arranged in rows as a function of the immersion time, these are shown in Figure 15. The SEM micrographs showed a slight change to the intermetallic over 16 hours. Larger SEM micrographs of the intermetallic after
4, 8 and 16 hours of immersion are shown in Figure 4.18. Careful examination of these micrographs shows that after 8 and 16 hours small particles or clusters of material have formed or have been deposited onto the surface of the intermetallic.

In addition to the clusters of material, there was a noticeable change in the roughness of the matrix surrounding the intermetallic. This extended up to 2 μm from the matrix/intermetallic interface. This indicated that there was some accelerated removal of matrix material from the intermetallic periphery. The most noticeable difference occurred between 8 hours and 16 hours of immersion. When the intermetallic was examined after 16 hours a significant corrosion feature was observed in the FOV. These effects are more clearly observed in the larger micrographs shown in Figure 4.18.

Examination of the SAM maps showed a similar trend as was observed for Intermetallic #1. The oxygen and aluminium intensity remained weak on the intermetallic until 8 hours of immersion. After which the intensity began to increase. After 16 hours, the aluminium and oxygen intensities on the intermetallic appeared to closely match the surrounding matrix. As with the previous intermetallic the oxygen and aluminium intensities begin to become intensified on the intermetallic after 8 hours, with a reduction in intensity observed on the matrix immediately adjacent to the intermetallic. As this occurs for Intermetallic #1 and Intermetallic #2 it is possible that part of this apparent increase in intensity is an artefact of the large drop in intensity from the matrix. This would act to artificially increase the intensity from the intermetallic centre in the maps as it remained flat. The decrease in intensity was a consequence of the increased surface roughness as the matrix began to corrode. Unlike Intermetallic #1, which showed a fairly uniform decrease in the oxygen and aluminium intensity, the decrease on Intermetallic #2 was more isolated to the matrix around the intermetallic. The matrix/intermetallic interface is where corrosion is likely to be most severe.

In the SAM maps collected after 16 hours the intensity of aluminium and oxygen are lowest at the interface between the intermetallic and the matrix. This is because material has been removed by the corrosion process. The sharp increase in the intensity of aluminium and oxygen, at this point, on the intermetallic indicates the deposition of corrosion products.

In the initial maps, prior to immersion in KCl, a feature was observed in the chromium map. This appeared to surround the intermetallic on three sides. It was also observed in the SEM micrograph. After 15 minutes immersion this feature was no longer observed in the chromium map or the SEM micrograph, it was also not observed in the initial x-ray map. This showed that it was a surface specific feature.
Figure 4.13 SEM micrographs (first row) and the SAM maps of Al, O, Fe, Cu, Cr, Mg and Si at different immersion times for Intermetallic #2.

After 15 minutes of immersion the intensity of the Cu LMM and Cr LMM peaks fell to such an extent that mapping became ineffective, showing only noise. The intensity of the Fe LMM Auger peak remained sufficiently high to enable continued monitoring by SAM analysis, the iron appeared to stay localised to the intermetallic throughout the immersion time. The Mg KLL and Si KLL peaks were not present with sufficient intensity to enable mapping until after 16 hours. At which point, their peaks were included in the SAM analysis. Following 16 hours of immersion a feature was observed in the bottom right of the SEM micrograph. This feature was believed to be the result of subsurface removal of material or volume expansion leading to the formation of a blister on the surface. The significant topography introduced by the blister distorted the mapping and introduced artefacts into the maps. This was most clearly observed in the bottom right of each of the maps after 16 hours. In these noise was observed in the maps. This was a result of shadowing at the surface which attenuates the electrons from this region of the surface.

To investigate the corrosion feature observed to the right of the intermetallic in the SEM micrographs a number of AES survey spectra were collected from Points 3, 4 and 5 shown in Figure 4.11 (b), these are shown in Figure 4.14. Points 3 and 4 were collected from the surface of the blister with a smooth appearance. They showed only aluminium and oxygen, indicating the blister was formed of an aluminium oxide layer. The spectrum from Point 4 had significantly weaker intensity than Point 3, as the analysis point was located behind topography on the surface. Point 5 was collected from the white material in the bottom right of the
SEM micrograph. This showed intense silicon and magnesium Auger transitions in addition to the aluminium and oxygen Auger transitions.

![AES spectra](image)

**Figure 4.14** AES point spectra from Points 3, 4 and 5, in Figure 4.11, from the region surrounding Intermetallic #2 after 16 hours of immersion.

Survey spectra that were collected from Point 1 on the centre of Intermetallic #2 after 45 minutes, 4 hours and 16 hours, are shown in Figure 4.15. Examination of the spectra collected after 45 minutes and 4 hours showed that the surface composition of the intermetallic had changed little compared to the initial survey spectra. The Fe LMM, Si KLL, Al KLL and O KLL peaks were all still observed and only showed a slight change in intensity. Over the course of 4 hours the thickness of the aluminium oxide layer appeared to remain fairly constant because the peak intensity ratio of the iron and aluminium peaks did not change significantly.

The most significant change on the surface occurs after 16 hours of immersion, at which point the spectrum showed that the Fe LMM peaks were no longer observed. Additionally, there was no effect of these peaks on the background, suggesting that iron was not present within the entire depth of analysis of AES. It was also noted that the carbon intensity had dropped considerably. This suggested that a layer of corrosion products, such as aluminium hydroxide, started to deposit onto the surface of the intermetallic after 16 hours. This correlates well with the SAM maps which showed an increase in the oxygen and aluminium concentration on the intermetallic after 16 hours.
4.4.3.3 EDX results as a function of time

The SEM micrographs together with the elemental EDX maps from Intermetallic #2, collected to provide information about the bulk composition are shown in Figure 4.16. They show that the bulk of the intermetallic remained unchanged throughout the immersion time, while the alloy adjacent to the intermetallic was corroded. The shape and size of the intermetallic in the transition metal maps and the size particle outline in the magnesium and aluminium maps did not change until 16 hours of immersion. After 8 hours of immersion the oxygen EDX map underwent a similar change in appearance as the oxygen SAM map, with the signal intensity becoming more diffuse and delocalised from the intermetallic. This showed that the surface was becoming rougher as the matrix was corroded. As with Intermetallic #1 the development of small pits were observed in the SEM micrograph and by the localised increase in intensity of oxygen x-rays in the EDX map at small points away from the intermetallic. A corresponding decrease in intensity for oxygen in the SAM maps was also observed.
EDX maps of the feature next to the intermetallic showed that the majority of the structure was concentrated in oxygen and chlorine, although a low concentration of aluminium was also present. While the chlorine was detected in the EDX maps it was not observed in the AES point spectra collected from this region. As the chlorine would have been in the form of aluminium chloride (AlCl$_3$), which is highly soluble in water, it would have been removed from the surface during the rinsing step before analysis. The absence of x-rays from the elements present in the bulk of the alloy, including magnesium, aluminium and zinc suggests that...
the blister is covering a void from which no x-rays are generated. Phase analysis was performed on the elemental x-ray maps and the resultant phases are shown in Figure 4.17. Quantification from each phase is shown in Table 4.5.

![Figure 4.17 Phase maps of the four phases produced from principle component analysis on the x-ray maps from Intermetallic #2 after 16 hours immersion.](image)

<table>
<thead>
<tr>
<th>Phase/Wt.%</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>Cr</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>Cl</th>
<th>K</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>1.5</td>
<td>86.5</td>
<td>ND</td>
<td>0.3</td>
<td>0.2</td>
<td>ND</td>
<td>1.8</td>
<td>7.1</td>
<td>0.2</td>
<td>ND</td>
<td>2.3</td>
</tr>
<tr>
<td>b</td>
<td>0.7</td>
<td>57.7</td>
<td>1.0</td>
<td>0.4</td>
<td>0.8</td>
<td>ND</td>
<td>0.4</td>
<td>2.1</td>
<td>5.0</td>
<td>0.4</td>
<td>30.7</td>
</tr>
<tr>
<td>c</td>
<td>11.0</td>
<td>26.7</td>
<td>22.3</td>
<td>ND</td>
<td>1.4</td>
<td>ND</td>
<td>0.6</td>
<td>1.4</td>
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<td>ND</td>
<td>34.8</td>
</tr>
<tr>
<td>d</td>
<td>0.5</td>
<td>63.3</td>
<td>0.3</td>
<td>4.2</td>
<td>14.9</td>
<td>0.7</td>
<td>8.3</td>
<td>3.8</td>
<td>0.2</td>
<td>ND</td>
<td>3.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Phase/At.%</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>Cr</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
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</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>1.7</td>
<td>89.9</td>
<td>ND</td>
<td>0.2</td>
<td>0.1</td>
<td>ND</td>
<td>0.8</td>
<td>3.0</td>
<td>0.2</td>
<td>ND</td>
<td>4.1</td>
</tr>
<tr>
<td>b</td>
<td>0.7</td>
<td>49.2</td>
<td>0.8</td>
<td>0.2</td>
<td>0.3</td>
<td>ND</td>
<td>0.4</td>
<td>0.7</td>
<td>3.3</td>
<td>0.3</td>
<td>44.2</td>
</tr>
<tr>
<td>c</td>
<td>10.0</td>
<td>21.9</td>
<td>17.6</td>
<td>ND</td>
<td>0.6</td>
<td>ND</td>
<td>0.2</td>
<td>0.5</td>
<td>1.0</td>
<td>ND</td>
<td>48.2</td>
</tr>
<tr>
<td>d</td>
<td>7.6</td>
<td>73.8</td>
<td>0.3</td>
<td>2.6</td>
<td>8.4</td>
<td>0.4</td>
<td>4.2</td>
<td>1.8</td>
<td>0.3</td>
<td>ND</td>
<td>7.6</td>
</tr>
</tbody>
</table>

The EDX phase analysis revealed four separate phases. Phase (a) consisted of the aluminium alloy matrix and quantification was consistent with the bulk alloy. The slight increase observed in the transition metal content was likely to be a result of the interaction volume overlapping with the intermetallic and that signal being grouped in with the rest of the matrix phase instead of producing an edge phase. Phase (b) was the blister feature which appeared to consist of aluminium, oxygen and chlorine. Based upon the absence of x-rays from this region, it appeared that the matrix under the blister was removed. The remaining material observed in the SEM micrograph and the phase map was caused by a thin capping layer of $\text{Al}_2\text{O}_3$, $\text{AlCl}_3$ and aluminium oxychlorides [84]. Despite being highly soluble in water and the sample undergoing a rinsing stage to remove remaining KCl from the corrosive solution, the aluminium chlorides are likely to have been able to remain associated with the feature as they were covered by a capping layer.

Phase (c) consisted of the white material that was observed in the bottom right of the SEM micrograph. This is most clearly observed in Figure 4.18 (c). AES spectra from this region showed significant amounts of
magnesium and silicon. The phase analysis as well as the raw x-ray maps showed that the material was a discreet particle separate to the rest of the feature. Quantification of the particle showed it to be MgSi₂ and Al₂O₃. Phase (d) was the intermetallic. The size and shape was the same as observed in the initial phase maps, indicating that the bulk of the intermetallic was unchanged during the investigation. Quantification of the phase showed that the concentrations of aluminium, iron and copper have changed. This was likely a result of including oxygen within this quantification.

Figure 4.18 shows a series of three enlarged SEM micrographs from Intermetallic #2. The SEM images show the intermetallic after (a) 4 hours, (b) 8 hours and (c) 16 hours of immersion. Throughout the time series small clusters of bright material, ~100-200 nm in diameter, begin to appear on the sample surface, gradually becoming more numerous after 8 and 16 hours. The micrograph after 8 hours also shows that there was enhanced attack to the matrix immediately surrounding the intermetallic. This enhanced corrosion extended ~2 µm from the intermetallic.

![Figure 4.18 Enlarged SEM images of Intermetallic #2 from (a) 4 hours, (b) 8 hours and (c) 16 hours of immersion.](image)

### 4.4.3.4 FIB cross sectioning

Intermetallic #2 was the first to be located within the FIB. The deposition of a protective platinum strap was attempted. However, it was found that, because of an ion gun fault, the surface of the intermetallic and blister were slightly milled by the platinum. Therefore, the deposition of protective straps on the other two intermetallics was not attempted. Figure 4.19 shows SEM micrographs of Intermetallic #2 after cross sectioning by FIB milling. The images revealed severe attack of the matrix at the interface of the intermetallic, as highlighted in Figure 4.19 (a). The crevices appeared to have some structure and directionality indicating that they may have been formed by intergranular corrosion. The matrix was most severely corroded in the region that was beneath the blister. Figure 4.19 (b) shows a rotated sample to help show the region under the blister. The matrix adjacent to the intermetallic showed the removal of considerably more material than Intermetallic #1.
4.4.4 Intermetallic #3

4.4.4.1 Initial analysis of the third intermetallic

The same analysis procedure was utilised for the third intermetallic as for Intermetallics #1 and #2. The surface was imaged using the SEM prior to exposure to KCl solution. The micrograph collected is shown in Figure 4.20 (a). The intermetallic was the largest of the three studied: being ~6 x 5 μm in size and more rounded than the two previous intermetallics. As with the previous intermetallics Points 1 and 2 in the figure denote the positions from which AES and EDX point spectra were collected. The EDX spectra from the intermetallic and the matrix are shown in Figure 4.21. From the EDX quantification the intermetallic type was believed to be Al₇Cu₂Fe.

Figure 4.21 (a) shows the EDX spectra collected from Intermetallic #3 and the nearby matrix. Quantification of the matrix matched that expected for the alloy. Quantification from each EDX spectrum is shown in Table 4.6. Intermetallic #3 contained the highest concentration of copper of the three. Figure 4.21 (b + c) show the phase maps produced from the raw x-ray maps. They show that within the analysis volume of the electron beam the intermetallic and the surrounding matrix are homogeneous and that the point spectra collected from Points 1 and 2 accurately represent the compositions of the intermetallic and the matrix. The phase maps
were generated from the x-ray maps collected after 45 minutes of immersion as EDX maps were not collected for this intermetallic for the first 45 minutes.

![Graph and EDX spectra](image)

**Figure 4.21** (a) EDX spectra collected from Intermetallic #3 and the local matrix, (b + c) EDX phase maps of the intermetallic and matrix. Their composition is shown in Table 4.6.

<table>
<thead>
<tr>
<th>Region/Composition</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>Cr</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intermetallic wt.%</td>
<td>0.2</td>
<td>50.6</td>
<td>ND</td>
<td>ND</td>
<td>12.0</td>
<td>1.5</td>
<td>33.9</td>
<td>3.0</td>
</tr>
<tr>
<td>Matrix wt.%</td>
<td>1.9</td>
<td>87.6</td>
<td>ND</td>
<td>0.4</td>
<td>ND</td>
<td>ND</td>
<td>1.8</td>
<td>8.4</td>
</tr>
<tr>
<td>Intermetallic at.%</td>
<td>0.3</td>
<td>71.1</td>
<td>ND</td>
<td>ND</td>
<td>8.0</td>
<td>0.9</td>
<td>18.3</td>
<td>1.7</td>
</tr>
<tr>
<td>Matrix at.%</td>
<td>2.2</td>
<td>93.1</td>
<td>ND</td>
<td>0.2</td>
<td>ND</td>
<td>ND</td>
<td>0.8</td>
<td>3.7</td>
</tr>
</tbody>
</table>

**Table 4.6 EDX quantification from Intermetallic #3 and the surrounding matrix**

4.4.4.2 AES and SAM results as a function of time

Intermetallic #3 showed the most noticeable change over the course of the investigation. Figure 4.22 shows the SEM micrographs and the SAM maps of Intermetallic #3. The initial SEM micrograph and the corresponding SAM maps show the intermetallic to be slightly smaller than the rest in the series, this was caused by a change in the operating magnification that was then maintained for the remainder of the investigation, as such the scale bar shown in the figure as 10 μm should be 12 μm for these images. Examination of the initial SEM micrograph showed a light halo surrounding the intermetallic, this halo was believed to be caused by topography at the interface caused by the preferential removal of the surrounding matrix during polishing. The light halo may also have been caused by the onset of initial corrosion caused by moisture on the surface from atmospheric exposure following polishing.

As was observed for the previous two intermetallics, small pits appeared on the matrix within the FOV. After 45 minutes the sharp edge observed in the aluminium map starts to blur, indicating some activity at the intermetallic/matrix interface. Although the copper and oxygen SAM maps still showed sharp edges of
intensity associated with the intermetallic. The halo feature surrounding the intermetallic also seemed to have disappeared, possibly because of deposition of corrosion products at the interface. The surface of the intermetallic appeared to remain smooth after 45 minutes of immersion. However, 2 hours a significant change was observed as the intermetallic was completely covered with clusters of material. This change in the surface was most noticeable in the oxygen and copper maps. The oxygen intensity which was poor in the 45 minute map showed a large increase in intensity on the centre of the intermetallic while the copper which was previously intense had reduced to such an extent it was no longer possible to map the peak. This showed that corrosion products had deposited onto the surface of the intermetallic, attenuating the previously intense copper Auger transitions.

The aluminium Auger maps track the oxygen maps closely. After 45 minutes the edges of the intermetallic defined by the low aluminium intensity blurred. After 2 hours, the region of low intensity grew and generally matched the outline of the deposited material observed in the SEM micrograph, except for a few small patches on the centre of the intermetallic. The silicon intensity was very weak in the SAM maps as the KLL Auger transition was mapped instead of the more intense Si LMM. This was performed to avoid problems with overlapping peaks and the secondary electron tail near the Si LMM which could contribute it the peak intensity. Silicon SAM maps were not acquired for the first 45 minutes of immersion as point spectra collected from the intermetallic did not show the Si KLL Auger transition. After 2 hours the maps show a slight increase in intensity in patches on the centre of the intermetallic. The dark noisy feature in the bottom centre of the all of the silicon maps was caused by the attenuation of electrons from this region by material deposited onto the intermetallic.

The copper Auger maps show a high concentration of copper at the surface of the intermetallic until 2 hours of immersion. After 2 hours copper was no longer observed. The absence of copper signal showed that the material deposited onto the surface of the intermetallic was thick enough after just 2 hours to attenuate the electrons generated by the intermetallic. The zinc Auger maps do not appear to show any activity until 45 minutes at which point, a slight increase in intensity was observed over the entire intermetallic. This signal then seemed to disappear when the corrosion products were deposited onto the intermetallic. Little change was observed to occur between 2 and 4 hours of immersion. The SEM micrographs and the Auger maps appeared almost identical. This may indicate that the intermetallic was in a passive state.

After 8 hours a thicker layer of material was observed to deposit onto the surface of the intermetallic. This was noted from the SEM micrographs. It was also apparent, after 8 hours, that the matrix surrounding the intermetallic had been severely corroded. A dark halo around the intermetallic was observed in the SEM micrograph. Additionally, the aluminium and oxygen Auger maps showed a drop in intensity from this region as the surface becomes rougher as material was removed by the corrosion process. An increase in the zinc intensity from the centre of the intermetallic was observed after 8 hours of immersion, which remained after 16 hours of immersion. The amount of deposited material and the size of the dark halo both seemed to increase after 16 hours of exposure. The initial clusters of deposited material appeared to have joined
together and completely covered the surface of the intermetallic. The significant preferential deposition of corrosion products onto Intermetallic #3 combined with the accelerated corrosion of the adjacent alloy showed that it was cathodic with respect the matrix.

Figure 4.22 SEM micrographs (first row) and the SAM maps of Al, O, Cu, Fe, Zn and Si at different immersion times for Intermetallic #3.

Figure 4.23 shows the survey spectra collected from Intermetallic #3 after 45 minutes, 4 hours and 16 hours of immersion. The spectrum collected after 45 minutes showed that the surface was still similar to the spectrum collected from the surface prior to immersion, the only noticeable change was the presence of a small Zn LMM peak. The spectrum collected after 4 hours showed that the transitions metal peaks were no longer present. However, silicon was observed. This fitted with the behaviour observed in the transition metal Auger maps, where the intensity on the intermetallic appeared to significantly decrease after 2 hours of immersion and was no longer apparent after 4 hours of immersion. The increase in the Si KLL, Al KLL and O KLL peak intensities, after 4 hours, indicated that the first corrosion products deposited onto the intermetallic were silicon dioxide and aluminium hydroxide. After 16 hours of immersion the spectrum changed significantly. The Si KLL was much weaker whilst the Al KLL and O KLL Auger transitions had significantly increased in intensity. Intense Zn LMM Auger peaks were observed, indicating that secondary corrosion products concentrated in aluminium and zinc are deposited onto the surface of the intermetallic after the initial silicon and aluminium deposits.
4.4.4.3 EDX results as a function of time

Figure 4.24 shows the SEM micrographs and the x-ray maps collected from Intermetallic #3. The aluminium and magnesium maps closely correlated throughout the investigation. After 2 hours of immersion the low intensity region in the aluminium and magnesium maps, representing the intermetallic, remained constant in size. However, after 4 hours the size of the low intensity region increased. This reached a maximum after 16 hours. There was also a wider region extending beyond the intermetallic into the matrix ~4 μm around the intermetallic where a slight decrease in intensity was observed. This suggested that alloy material which would otherwise produce aluminium and magnesium x-rays had been removed by corrosion.

The initial oxygen x-ray map after 45 minutes shows less intensity associated with the intermetallic, which is expected as the oxygen is not part of the intermetallic composition. The most intense region of x-rays is located at the interface between the matrix and the intermetallic. After 2 hours the oxygen intensity was isolated to small clusters of material on the intermetallic. These clusters remain in the same position for the remainder of the investigation. They appeared to consist of oxygen and silicon as they are only observed in the silicon and oxygen maps. This indicated that the initial corrosion products consisted of silicon dioxide. As well as the clusters, the oxygen intensity appeared to slightly increase on the matrix after 2 hours. This region gradually increased in size and moved out onto the matrix throughout the immersion time, indicating corrosion of the adjacent matrix.

The zinc x-ray maps showed a slight depletion in intensity in the central region of the intermetallic, this is more noticeable after 2 and 4 hours of immersion as the corrosion products deposited onto the surface attenuate the zinc x-rays that were produced. After 8 hours there was a sharp increase in the intensity of zinc from the intermetallic. This was also apparent in the map collected after 16 hours. These regions of intensity appeared to be located in between the regions previously coated with the oxygen and silicon containing clusters. This suggested that some of the later corrosion products were rich in zinc. The iron, copper, chromium and nickel x-ray maps showed no change in the size or shape of the central region of intensity associated with the intermetallic, in fitting with the survey spectra collected from the surface after 16 hours. The slight decrease in x-ray intensity that was observed in patches of the intermetallic region was a result of...
greater attenuation of the generated x-rays by the corrosion products that deposited onto the surface of the intermetallic.

Figure 4.24 SEM micrographs (first row) and the x-ray maps of Al, O, Fe, Cu, Cr, Ni, Zn, Si and Mg at different immersion times for Intermetallic #3.
Phase analysis was performed on the x-rays maps from Intermetallic #3 and the results are shown in Figure 4.25 with the corresponding quantification shown in Table 4.7. Four different phases were observed as a result. Phase (a) was the matrix surrounding the intermetallic, quantification showed it to be consistent with that expected for the matrix. Phase (b) represents the matrix region immediately adjacent to the intermetallic. This region is the most severely corroded and an increase in the oxygen concentration is observed, this is likely to be a result of the increased surface roughness as material is not removed uniformly. Phases (c) and (d) represent a mix of the intermetallic composition and additional corrosion products that have deposited onto the surface of the intermetallic. Phase (c) shows the central region of the intermetallic, quantification shows that it contains a greater concentration of copper and less oxygen than phase (d). The increased concentration of oxygen at the rim of the intermetallic suggests that the deposition of corrosion products is greatest around the rim of the intermetallic.

![Figure 4.25 EDX phase maps of Intermetallic #3 after 16 hours of immersion.](image)

<table>
<thead>
<tr>
<th>Phase/ Wt.%</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>Cr</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>Cl</th>
<th>O</th>
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<tbody>
<tr>
<td>a</td>
<td>1.7</td>
<td>84.3</td>
<td>ND</td>
<td>0.3</td>
<td>0.1</td>
<td>ND</td>
<td>2.0</td>
<td>7.9</td>
<td>ND</td>
<td>3.7</td>
</tr>
<tr>
<td>b</td>
<td>1.3</td>
<td>76.0</td>
<td>0.2</td>
<td>0.5</td>
<td>0.4</td>
<td>0.1</td>
<td>2.9</td>
<td>9.9</td>
<td>ND</td>
<td>8.3</td>
</tr>
<tr>
<td>c</td>
<td>0.3</td>
<td>45.7</td>
<td>1.5</td>
<td>0.1</td>
<td>8.8</td>
<td>1.0</td>
<td>28.2</td>
<td>6.4</td>
<td>0.1</td>
<td>8.0</td>
</tr>
<tr>
<td>d</td>
<td>0.6</td>
<td>51.3</td>
<td>3.3</td>
<td>0.3</td>
<td>5.3</td>
<td>0.4</td>
<td>17.5</td>
<td>6.9</td>
<td>0.1</td>
<td>13.8</td>
</tr>
<tr>
<td>At.%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>2.0</td>
<td>87.1</td>
<td>ND</td>
<td>0.2</td>
<td>0.1</td>
<td>ND</td>
<td>0.8</td>
<td>3.4</td>
<td>ND</td>
<td>6.5</td>
</tr>
<tr>
<td>b</td>
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<td>78.2</td>
<td>0.2</td>
<td>0.3</td>
<td>0.2</td>
<td>0.1</td>
<td>1.2</td>
<td>4.2</td>
<td>ND</td>
<td>14.2</td>
</tr>
<tr>
<td>c</td>
<td>0.3</td>
<td>57.0</td>
<td>1.8</td>
<td>0.1</td>
<td>5.3</td>
<td>0.6</td>
<td>14.9</td>
<td>3.3</td>
<td>ND</td>
<td>16.7</td>
</tr>
<tr>
<td>d</td>
<td>0.7</td>
<td>56.0</td>
<td>3.5</td>
<td>0.2</td>
<td>2.8</td>
<td>0.2</td>
<td>8.1</td>
<td>3.1</td>
<td>ND</td>
<td>25.4</td>
</tr>
</tbody>
</table>

**4.4.4.3 FIB cross sectioning**

Peripheral pitting or 'trenching' was observed on the matrix encompassing the intermetallic [95]. This accelerated removal of material around Intermetallic #3 was apparent after examination of the SEM micrographs collected after cross sectioning by FIB milling, as shown in Figure 4.26. The trench surrounding the intermetallic extends ~2.5 μm into the matrix and is ~2 μm deep at the matrix/intermetallic interface. The surface of the intermetallic is proud of the surface. Close examination of the surface of the intermetallic...
reveals an open, porous structure formed by the deposited corrosion products. The aluminium matrix in the trench also appears to have a porous structure.

![SEM micrograph of Intermetallic #3 after FIB milling with the intermetallic and the associated trench marked.](image)

**4.4.5 Diagnosis of galvanic activity by cation precipitation**

To determine if the intermetallics were acting as cathodes with respect to the matrix and estimate their cathodic current density, the sample was sequentially immersed in solutions of magnesium chloride with concentrations of 0.001 M, 0.01 M and 0.1 M for 15 minutes. This was performed after the corrosion investigation was completed but before FIB milling. Magnesium chloride is highly soluble in water while magnesium hydroxide is highly insoluble in water. This allows the marking of the surface at cathodic regions by the deposition of magnesium hydroxide. When magnesium chloride is dissolved the ions disassociate and the positively charged Mg$^{2+}$ ions are attracted to the negatively charged regions of the surface. The cathodic regions of the surface produce OH$^-$, hydroxyl ions. These are produced as part of the electrolysis of water because at the electrons generated at the anode are consumed at the cathode by the reduction of water to hydroxyl ions. When the magnesium ions react with the hydroxyl ions, magnesium hydroxide, Mg(OH)$_2$ is formed and because it is so insoluble in water, $1.4 \times 10^{-4}$ M, it is immediately deposited coating the cathodic region of the surface.

By looking for magnesium in the spectra collected from the surface it is possible to accurately identify the cathodic regions of a surface [56]. Exposing the sample to increasing concentrations of magnesium chloride enables the bracketing of the critical concentration at which magnesium hydroxide precipitates onto the cathodic area which brackets the cathodic current density. Figure 4.27 shows spectra collected from the centre of each of the intermetallics after exposing the sample to the different solutions. Intermetallics #1 and #2 did not show the presence of any magnesium over the tested concentration range. It is possible that the corrosion feature that appeared after 16 hours of immersion near Intermetallic #2 had an effect on the results of this test. Intermetallic #3 showed a weak but observable Mg KLL peak after exposure to the 0.1 M magnesium chloride solution. The Auger peak was located at ~1180 eV, which is consistent with magnesium hydroxide. The presence of magnesium showed that Intermetallic #3 was cathodic to the surrounding alloy. The absence of magnesium on Intermetallics #1 and #2 does not exclude the possibility that they were
cathodic with respect to the matrix. It may be that they cannot support a corrosion current density large enough to deposit magnesium hydroxide at the concentrations tested.

To calculate the cathodic current density that is bracketed Equation 3.1 is used.

\[
\frac{i}{A} = \frac{F}{\delta} \left( D_{OH} \left( \frac{K_{sp}[Mg]}{[H]} \right)^{0.5} - K_w \left( \frac{[Mg]}{K_{sp}} \right)^{0.5} \right) + D_{H} \left( [H] - K_w \left( \frac{[Mg]}{K_{sp}} \right)^{0.5} \right)
\]  

(3.1)

Where:

F is Faradays constant, \(D_{OH}\) and \(D_{H}\) are the diffusion coefficients for hydroxyl ions and hydrogen respectively, \(K_{sp}\) is the solubility product for magnesium hydroxide, \(K_w\) is the ionic product for water and \(\delta\) is the diffusion distance, taken as twice the radius of intermetallic.

The radius of Intermetallic #3 was taken to be 2.5 μm, from the SEM micrograph. A pH 7 solution was used, a diffusion coefficient for hydroxyl ions of \(0.52 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}\) was used and the magnesium hydroxide solubility product was taken as \(5 \times 10^{-11}\). A work through of the equation used to calculate the current density of the intermetallic is shown below for one of bracketed current densities:

\[
\frac{i}{A} = \frac{9.65 \times 10^4}{5 \times 10^{-6}} \left( 0.52 \times 10^{-8} \left( \frac{1.8 \times 10^{-11}}{0.1} \right)^{0.5} - 1 \times 10^{-14} \right) + 0.93 \times 10^{-8} \left( 1 \times 10^{-7} - 1 \times 10^{-14} \left( \frac{0.1}{1.8 \times 10^{-11}} \right)^{0.5} \right)
\]

\[
\frac{i}{A} = 1.93 \times 10^{10} \left( 0.52 \times 10^{-8} \left( 1.34 \times 10^{-5} - 1 \times 10^{-7} \right) \right) + 0.93 \times 10^{-8} \left( 1 \times 10^{-7} - 7.45 \times 10^{-10} \right)
\]

\[
\frac{i}{A} = 1.93 \times 10^{10} \left( 0.52 \times 10^{-8} \left( 1.33 \times 10^{-5} \right) + 0.93 \times 10^{-8} \left( 9.92 \times 10^{-8} \right) \right)
\]

\[
\frac{i}{A} = 1.93 \times 10^{10} \left( 6.92 \times 10^{-14} + 9.23 \times 10^{-16} \right)
\]

\[
\frac{i}{A} = 1.33 \times 10^{-3} \text{ A m}^2
\]
4.5 Discussion

4.5.1 General discussion and observations

Examination of the surface of a 7075 aluminium alloy showed the presence of significant number of second phase particles, aligned with the working direction of the alloy. These ranged in size from 0.1-30 μm. EDX analysis of the intermetallic particles showed them to be rich in aluminium, copper, iron and silicon, compared to the matrix. Auger analysis of the surfaces showed a mix of aluminium oxide and transition metals. Three intermetallics were studied and the progressive change in corrosion behaviour of each was monitored over time. The galvanic activity of the particles was determined by inspection of the intermetallics and the surrounding alloy in the SEM micrographs, AES point spectra and by the deposition of magnesium hydroxide on their surface.

A 15 keV primary beam energy was utilised during the x-ray analysis. This energy was chosen because it would provide a significant cross section for the higher energy transition metal Kα transitions while still minimising the interaction volume. The depth of analysis was investigated using the Monte-Carlo and Phi-Rho-Z simulator Win X-ray V1.3 [78]. An approximate analysis depth of the 15 keV beam was found to be ~1.5 μm within the intermetallic. A larger depth of analysis, ~1.8 μm, was found for the alloy because of the comparatively lower atomic mass. In each case this depth of analysis was taken as the maximum depth from which the generated Al Kα x-rays could be emitted.

Traces of zinc and magnesium were present in all of the EDX spectra collected from the intermetallics. This suggests that these elements were present in small quantities in the intermetallics or that there was some degree of x-ray fluorescence from the intermetallic exciting the surrounding matrix. This could result from the transition metal Kα x-rays emitted by the intermetallic, going on to excite the lower energy Mg Kα and Zn Lα x-rays in the surrounding alloy, making it appear that they were present in the intermetallic.

Despite not observing their peaks in the AES point spectra the chlorine and potassium kinetic energies where included in SAM mapping for each of the intermetallics. The maps produced from this data showed only noise. The absence of the peaks does not indicate that they were not present, merely that for the given analysis time no peak could be ascertained above the noise and so, if present, the concentration was below the detection limit.

4.5.2 User beware - a cautionary tale

The danger of blindly accepting what the "computer says" was encountered within this work. This has been provided as evidence to always manually interrogate data following acquisition and as a warning that while automated analysis and data processing routines are exceedingly advanced they do not replace the user.

After the initial processing of the raw count maps from Intermetallic #3, following 16 hours of immersion, into principle component phase diagrams an artifact is observed. Without further thought and input from the user this artifact can easily be interpreted as real data. Figure 4.28 (a-e) shows the phase maps produced
while fully reliant upon the automated principle component analysis software whereas (f-i) shows the phase maps following intervention from the user. It can be seen that phase (b) and phase (c) have been merged to form the single phase (g) in the second set of maps. The reason for the artifact is the large reduction in signal intensity of the high wavelength, low energy, x-rays from this region of surface. These x-rays are attenuated by the corrosion products on the surface of the intermetallic, causing a change in the ratio between the lower energy and the higher energy x-ray peaks. This leads the software to believe that another phase is present when it is only an artifact of the detector geometry and the sample orientation.

![Phase maps](image)

**Figure 4.28** Phase maps of Intermetallic #3 following 16 hours of immersion: Maps (a-e) produced without user intervention, maps (f-i) produced following intervention to remove an artifact phase.

4.5.3 Intermetallic #1

Using the quantification provided by EDX, Intermetallic #1 was believed to be an Al$_{12}$Fe$_3$Si type intermetallic. While this type of intermetallic is known to form in aluminium alloys and most accurately reflects the EDX data it is possible given the vast number of possible compositions of intermetallics that this is incorrect and a better description of the intermetallic would be as an Al-Fe-Si intermetallic [96].

AES survey spectra collected from the centre of the intermetallic after 45 min, 4 hours and 16 hours of immersion showed little change in the surface composition. The only noticeable differences between the spectra collected prior to immersion and those collected after 16 hours was the slight drop in the intensity of the Fe LMM peaks relative to the Al KLL and O KLL peaks and the change in the background following the iron peaks. The indication from these observations was that the thickness of the oxide/hydroxide layer had increased or there had been some dissolution of iron from the surface of the intermetallic. It is less likely that a thin layer of deposited material was coating the intermetallic as the intensity of the C KLL and Si KLL peaks remained constant throughout the investigation.

Examination of all of the analysis data showed no evidence of cathodic or anodic activity of the intermetallic with respect to the matrix. The intermetallic was not observed to actively dissolve and no corrosion products were deposited onto the surface. Additionally, the test for cathodic activity by cation deposition from magnesium chloride solution showed no magnesium to be present on the intermetallic. This evidence supported the belief that Intermetallic #1 was not galvanically active with respect to the matrix. General
corrosion and small pits were observed on the surrounding matrix. However, corrosion did not appear to have been accelerated by the intermetallic. Despite the absence of apparent galvanic activity, corrosion was observed in the form of a crevice at the interface between the intermetallic and the matrix. This crevice was most clearly observed in the oxygen x-ray map collected after 16 hours, as the dark ring outlining the intermetallic. The final SEM micrographs, as well as the SEM micrographs collected after ion beam milling clearly showed this crevice. These micrographs were of superior quality and were collected with the recently installed JEOL-7100F SEM which was not available at the start of the investigation.

It is expected that if the experiment was continued, before ion milling the intermetallic, the eventual crevice would completely undercut the intermetallic and it would become detached from the matrix.

4.5.4 Intermetallic #2

Using the quantification provided by EDX, Intermetallic #2 was believed to be an Al$_7$Fe$_2$Cu type intermetallic. This composition matched well with the EDX data.

Careful examination of the enlarged SEM micrographs from Intermetallic #2 showed the formation of small clusters of material ~100-200 nm in diameter on the surface of the intermetallic. These could be seen as a parallel to the behaviour of Intermetallic #3 in which larger clusters ~200-500 nm in diameter were observed on the surface after 2 hours of immersion. The survey spectra collected from Intermetallic #2 showed that even after 4 hours of immersion there appeared to be little change to the surface. However, after 16 hours the intensity of the aluminium and oxygen peaks increased and the iron Auger transitions were no longer observed. Combining this observation with the apparent removal of carbon from the surface, as well as the clusters of material, suggested that corrosion products began to deposit onto the surface of the intermetallic after 8 hours of immersion.

Examination of all of the analysis data showed no evidence for anodic activity of the intermetallic with respect to the matrix. Careful examination of the SEM micrographs and consideration of the point AES spectra collected from the intermetallic after 16 hours showed some evidence for the deposition of corrosion products on the intermetallic. Although there was no magnesium detected on the intermetallic after exposure to the magnesium chloride solutions, based upon the apparent deposition of corrosion products on the surface it is possible that the intermetallic was cathodic but that the cathodic current density of the intermetallic was insufficient to cause the precipitation of magnesium hydroxide at the concentrations tested. Accelerated corrosion of the matrix immediately adjacent to the intermetallic is observed. A crevice was formed at the matrix/intermetallic interface but there was also evidence from the SEM micrographs and the SAM maps that this crevice was less abrupt because the matrix sloped down to the intermetallic and the surface was not parallel to the surface of the intermetallic as was observed for Intermetallic #1. The more dramatic crevicing observed in the SEM micrograph following cross sectioning by FIB was probably a result of the slight cathodic activity of the intermetallic with respect to the matrix.
As for Intermetallic #1, if the immersion time was continued it is possible that the intermetallic would be undermined and removed from the matrix. This is even more likely for the second intermetallic based upon the severity of the undercutting and crevicing observed around and underneath the intermetallic from the micrographs collected after ion milling. This evidence supported the idea that Intermetallic #2 was galvanically active to the matrix and was acting as a cathode.

### 4.5.5 Intermetallic #3

The third intermetallic was shown to be galvanically active to the surrounding matrix. It contained three times as much copper as Intermetallic #2. Corrosion products containing oxygen and silicon were observed to build-up in clusters on the surface after 2 hours of immersion. The oxygen maps and SEM micrographs indicated that corrosive attack was concentrated around the matrix surrounding the intermetallic, resulting in dissolution of the aluminium alloy. The formation of a trench surrounding the intermetallic was observed in the SEM micrographs and in the magnesium and aluminium EDX maps.

Zinc rich corrosion products, likely to be zinc hydroxide, were observed to deposit onto the surface of the intermetallic after 8 hours. This was shown in the SAM maps as well as the AES point spectra collected after 16 hours of immersion. It is believed that corrosion products containing silicon and aluminium were initially deposited onto the surface followed by products containing zinc and aluminium. This occurred once the trench began to form and the alloy surrounding the intermetallic was actively dissolved. As well as the visual evidence from the SEM micrographs, magnesium hydroxide deposition was confirmed by the presence of magnesium on the intermetallic after exposing it to the 0.1 M MgCl₂ solution. This showed that deposition occurred at some concentration of magnesium chloride between 0.01 M and 0.1 M. This brackets the cathodic current density to be between 1.3 and 4.3 μA cm⁻².

Consequently, in agreement with existing literature, the results confirmed that the Al₇Cu₂Fe type intermetallics behaved as cathodes to the surrounding alloy matrix [90,92,95]

### 4.6 Conclusions

The first intermetallic investigated, which was believed to be Al₁₂Fe₃Si, appeared to not be involved in micro-galvanic corrosion. However, crevice corrosion was observed at the interface between the matrix and the intermetallic.

The second intermetallic that was investigated, which was believed to be Al₁₂Fe₁₅Cu, appeared to be cathodically active with respect to the matrix. Severe crevice corrosion was observed at the interface between the matrix and the intermetallic. The second intermetallic (Al₁₂Fe₁₅Cu) was observed to be less cathodic than the third intermetallic (Al₁₇Cu₂Fe).

The third intermetallic investigated, which was believed to be Al₁₇FeCu₂, was shown to act as a cathode to the surrounding alloy, resulting in trenching of the local matrix.
Al(OH)$_3$, SiO$_2$ and Zn(OH)$_2$ corrosion products were observed to accumulate on the surface of the Al$_7$FeCu$_2$ intermetallic. Al(OH)$_3$ was also believed to gradually accumulate on the Al$_7$Fe$_2$Cu intermetallic.

The investigation showed that the corrosion behaviour of the second phase particles in AA7075 varied significantly with the composition of the particle. As such, a range of particle types must be examined within the metal to understand all of the different corrosion processes occurring at the metal surface.

Following the successful analysis of individual second phase particles, with different compositions and associated corrosive behaviour, in the same geometry and the establishment of a suitable working protocol it was decided to progress to the study of beryllium. The analysis of beryllium and beryllium compounds using, electron and x-ray spectroscopies is described in the next chapter. This investigation functions as the precursor to the corrosion study of beryllium.
Chapter 5 - The Electron and X-ray Spectra of Beryllium and Beryllium Compounds

5.1 Introduction

Following completion of the literature review, it became clear that wide range of second phase particles were present in beryllium with different sizes, morphologies and compositions. Therefore, it was decided that a thorough investigation of the microstructure was required prior to the corrosion investigation of beryllium. Additionally, no high quality reference spectra of beryllium or beryllium compounds were available.

5.2 Scanning electron microscopy

To image the surface of beryllium with a high spatial resolution and perform electron and x-ray analysis, two scanning electron microscopes were used in this project. The JEOL-7100F fitted with a triple microanalysis suite provided the clearest micrographs of the sample surface as well as the ability to perform WDX analysis and rapid EDX analysis on the samples. The MICROLAB 350 provided lower quality micrographs but allowed for the acquisition of Auger spectra and EDX spectra from the same regions of the sample surface during the corrosion investigation.

When using metal sample holder clips on the sample and metal tools to manipulate the sample, there is a risk of scratching or damaging the sample surface. This could result in the uncontrolled release of beryllium particulates in an uncontained environment. Therefore, the usual method of using sprung copper-beryllium clips to secure the sample for SEM analysis was avoided wherever possible. Instead, a small quantity of conducting silver paint was deposited onto the sample holder and the beryllium sample pressed onto the drop. The sample holder was then placed in a vacuum desiccator for ten minutes to allow the paint to outgas and dry, sticking the sample to the holder.

An SEM micrograph of the surface of a beryllium specimen is shown in Figure 5.1. A number of regions have been highlighted that represent common features on the sample:

1) Pores in the surface. These are produced in one of two ways. As holes left after the removal of second phase particles by the mechanical action of polishing/grinding or during hot isostatic pressing (HIP) through the incomplete densification of the beryllium powder.

2) A “glow” caused by subsurface second phase particles. The particles produce a greater number of backscattered electrons compared to the surrounding beryllium matrix, causing them to appear particularly bright.

3) Small particles decorate the grain boundaries. These small particles are predominately beryllium oxide. The thin oxide layer that forms on the surface of the beryllium feedstock powder is not dissolved during the HIP process and so the oxide remains distributed along the grain boundaries as small particles.
Second phase particles are found either at grain boundaries or less commonly within the beryllium grains. They are formed via precipitation during HIP, are already present within the beryllium feedstock powder or they are introduced during various processing stages.

The “glow” associated with many second phase particles is shown in Figure 5.2. The contrast has been reduced to help show the entire structure of the intermetallic. A large proportion of it is subsurface with a layer of beryllium covering it, this is shown by the lighter grey region in the micrograph. The two brighter regions are from the exposed intermetallic at the surface. In this case the intermetallic is the precipitate AlFeBe$_4$.

An effect that is often observed when imaging surfaces in an electron microscope is a “black box”. The black box is the result of the electron beam pyrolysing carbon on the sample surface which produces a thin layer of amorphous carbon. Figure 5.3 shows an example of a typical black box on beryllium. Despite the pressure in the JEOL 7100 SEM being maintained at a near constant $1 \times 10^{-6}$ mbar, the effect is still pronounced on beryllium.
Whilst the effect is often observed during imaging and analysis for most materials it is not much of a problem and does not normally interfere with the imaging of a higher atomic mass sample, such as steel. However, because of the particularly low excitation cross section of beryllium, the surface is quickly obscured by the thin carbon layer. The carbon, having a higher atomic mass, attenuates the low energy secondary, imaging, electrons from beryllium. The majority of the pyrolised carbon on the surface after imaging is believed to originate from the sample surface and not from the vacuum [97]. However, laboratory practices utilising the communal JEOL SEM were changed so as to not allow the analysis of freshly mounted metallurgical samples in resins or epoxy prior to an initial degassing stage in a vacuum desiccator. Additionally, the use of adhesive carbon tabs for sample mounting and the use of conductive adhesive tape were minimised. This change led to a dramatic improvement in the imaging performance of the microscope, as the amount of carbon deposited onto samples during imaging and analysis was significantly reduced. In addition to the previous changes, it was decided that prior to any SEM analysis, the contamination layer formed during polishing should be removed using an ozone cleaner. Following removal of the contamination by ozone cleaning the beryllium samples could be examined for long periods of time, at low beam energies and for EDX maps without the deposition of significant amounts of carbon. The effect of the UV-Ozone cleaner and how it works will be further discussed in Chapter 7.

5.3 Energy dispersive x-ray spectroscopy

5.3.1 Background

The depth of analysis in EDX was briefly touched upon in Chapter 3 but not fully discussed. In this chapter the depth of analysis has been taken as the depth from which the generated x-rays are able to escape the sample surface. This is different to the interaction volume which represents the entire scattering envelope of the primary electron beam. The attenuation length of x-rays is much greater than electrons of the same kinetic energy. For example, the Be KLL electrons, with a kinetic energy of 100 eV, have an attenuation length of ~0.5 nm. This is much less than the attenuation length of Be Kα x-rays, with a kinetic energy of 110 eV, which is ~200 nm. Each attenuation length was calculated in a beryllium matrix.
An approximation for the size of the interaction volume of a primary electron beam in a material can be acquired by performing Monte-Carlo calculations of the electron cascade within the chosen material. For this purpose Win X-ray was used [78]. Figure 5.4 shows the emitted x-ray envelopes for Be Kα, Al Kα and Fe Kα x-rays generated within an AlFeBe₄ precipitate using a 15 keV beam energy. The image highlights how, despite the interaction volume (black line) being particularly large, x-rays are not detected from all of the elements within the volume. The red line shows the depth and position from which the Be Kα x-rays are able to escape from the surface. Although the x-rays are excited from the majority of the interaction volume, the depth of analysis for the beryllium x-rays is determined by the attenuation length of the x-ray, which is ~200 nm for the AlFeBe₄ precipitate. The blue line is the region from which Al Kα x-rays are able to escape the surface, which is much deeper than Be Kα x-rays because of their higher energy. The depth of analysis for aluminium is again determined by the attenuation length of the x-rays in the material. The depth of analysis for Fe Kα is observed to be less than Al Kα. This is because the maximum depth of excitation and not the attenuation length of the high energy Fe Kα x-rays determine the depth of analysis. The maximum depth of excitation is the point at which electrons from the primary beam no longer have sufficient kinetic energy to excite Fe Kα x-rays.

Table 5.1 shows the approximate depths of x-ray generation for beryllium and for the AlFeBe₄ precipitate. The values in the table highlight the increased attenuation of x-rays within the higher atomic mass precipitate compared to beryllium. The values are based upon simulations using a 15 keV beam energy, 5000 electrons and a beam diameter of 20 nm. The interaction depth was taken as the area in which 95% of the electrons are located, this does not represent the total area from which those electrons can actually excite a given x-ray transition. For example, once a 10 keV primary electron has reached 95% of the penetration depth it will not retain all of the initial kinetic energy and as such it cannot excite many of the transition metal Kα transitions. The calculations were performed assuming a homogeneous distribution of the elements in the material.
Table 5.1 Depths of analysis vs. interaction depths for beryllium and AlFeBe₄

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (g cm⁻³)</th>
<th>Interaction depth (nm)</th>
<th>Depth of analysis for various x-rays (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>1.85</td>
<td>3000</td>
<td>Be Kα 1500  Al Kα 3000  Fe Kα 2000</td>
</tr>
<tr>
<td>AlFeBe₄</td>
<td>3.5</td>
<td>1800</td>
<td></td>
</tr>
</tbody>
</table>

5.2.2 Beryllium analysis

In Chapter 3 the Bremsstrahlung background was discussed. An example of a stainless steel was given where the background was a minor part of the total spectrum, with the large transition metal peaks superimposed on a low background. For beryllium, the Bremsstrahlung becomes the dominate part of the spectrum, with small elemental peaks observed on the background. A single example of a beryllium sample excited with a 15 keV beam was shown in Chapter 3, however shown in Figure 5.5 are x-ray spectra from beryllium excited using multiple beam energies. The figure shows the spectra recorded from a 1 mm² area, providing an averaged bulk analysis for beryllium. The spectra have not been normalised and are plotted on the same intensity scale, albeit offset in “y”. The spectra include one collected with a beam energy of 1 keV. At this beam energy the depth of interaction is ~15 nm, as primary electrons with such a low kinetic energy are quickly attenuated. Shown in Table 5.2 are the EDX quantification results from the EDX spectra in Figure 5.5, they were generated using Thermo Scientific Noran System Seven software.

By examining the spectra and the EDX quantification it is shown that for the 1 keV beam energy the majority of the signal is generated from the carbonaceous contamination and the beryllium oxide at the sample surface. This fits well with the expected depth of analysis for 1 keV electrons. However, a curiosity is observed: The native oxide on beryllium is BeO, a 1:1 mix of beryllium and oxygen that is ~3 nm thick, despite this, when examining the spectrum and the subsequent quantification this cannot be concluded. The concentration of oxygen was recorded as 87.5 at.% while beryllium was only 0.6 at.% and carbon 11.9 at.%. Even for the subsequent data sets with much greater depths of analysis the amount of beryllium inferred from the quantification is far from the true value. At 15 keV, the interaction depth in beryllium is >2.5 μm and so the thin carbon contamination and oxide layer should only correspond to <2% of the electron cascades path.
Highlighted here is the problem with quantifying light elements in EDX and how the normalisation of the analysis data to be 100% obscures poor quantification of the ultra-light elements.

Table 5.2 EDX quantification from the spectra shown in Figure 5.5

<table>
<thead>
<tr>
<th>Beam energy (keV)</th>
<th>EDX quantification at. % (normalised)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Be</td>
</tr>
<tr>
<td>1</td>
<td>0.6</td>
</tr>
<tr>
<td>3</td>
<td>20.4</td>
</tr>
<tr>
<td>5</td>
<td>35.0</td>
</tr>
<tr>
<td>10</td>
<td>61.3</td>
</tr>
<tr>
<td>15</td>
<td>61.6</td>
</tr>
</tbody>
</table>

Previously discussed in Chapter 3 was that as the atomic number decreases an excited atom is less likely to generate an x-ray because the dominant process for atomic relaxation switches from x-ray florescence to Auger electron emission. The result is a less intense signal from the light elements. Additionally, x-rays generated by light elements have a longer wavelength, are lower energy and so are more easily absorbed in the sample than shorter wavelength, higher energy x-rays. The majority of the x-rays produced by the light elements in the sample are absorbed by the sample itself, as such most x-rays that reach the detector come from near the surface of the sample, where they are strongly influenced by surface layers and contamination. This explains why the quantification and the spectrum for beryllium, even at 1 keV, show little beryllium, the majority of the x-rays are absorbed by the thin oxide layer and the surface carbon contamination.

5.2.3 Secondary phase particle analysis

Tuning the primary beam energy to a suitable value enables the isolation of the analysed volume to a particle of interest within the beryllium matrix. Phi-Rho-Z simulations using beam energies of 3-5 keV show that the depth of analysis is limited to the particle of interest if it is larger than ~1 μm. This is true even if the error in the simulation is 100%.

This allows the elements of the intermetallic to be examined with much less interference from the surrounding matrix material. It is unlikely that particles can be completely isolated from the matrix signal because even at low primary beam energies, secondary x-ray fluorescence caused by the x-rays that are emitted from an intermetallic would be able to excite x-rays from the surrounding matrix.

Figure 5.7 shows a range of typical EDX spectra collected from different inclusions found in beryllium. These include: BeO, Be₃N₂, Al₂O₃, elemental Si, Ti₃Si and AlFeBe₄. The Be Kα is not clearly observed in the EDX spectra for the oxide and the nitride as the O Kα and N Kα peaks particularly intense. This results in the Be Kα appearing weak and close to the spectrum baseline. The elemental silicon spectrum does not show a Be Kα peak as these inclusions do not have beryllium within them. Although the spectra were collected with low beam energy, to try and isolate the intermetallics from the matrix, it is best practice to make use of a combination of low and high beam energies.
Chapter 5

The Electron and X-ray Spectra of Beryllium

Christopher F. Mallinson

Figure 5.7 Typical EDX spectra from a range of second phase particles in beryllium, collected using a 3 keV beam energy. In addition to probing further into the bulk of an inclusion, the use of the higher beam energy above the appearance potential of higher Z elements can be useful for detecting trace impurities, an example of this is shown in Figure 5.8. Here the same AlFeBe₄ precipitate has been analysed using high and low primary beam energies, 15 keV and 3 keV respectively. Beryllium, carbon, oxygen, aluminium silicon and iron are observed to be present in the spectrum collected using a low beam energy. The spectral resolution in EDX is insufficient to reveal the Cr Lα and Mn Lα x-ray lines that are present. Their presence is only confirmed using the higher beam energy. The spectrum collected using the 15 keV beam shows the Cr Kα and Mn Kα peaks.

Figure 5.8 EDX spectra collected from the same AlFeBe₄ precipitate as in Figure 5.7, analysed using a 3 keV and 15 keV beam energy.
The minimum detectable concentration parameter influences the spectrum quality greatly for beryllium containing materials. Shown in Figure 5.6 are the EDX spectra from an AlFeBe₄ precipitate collected with acquisition times of 5 seconds and 1 minute. Although beryllium is not observed in the short acquisition time, sufficient counts are collected in 1 minute so that a distinct beryllium peak is observed. The difference in the spectra highlights the usefulness of extended acquisition times on regions of interest to increase the minimum detectable concentration of an element.

Figure 5.6 Two EDX spectra collected from the same AlFeBe₄ precipitate with different acquisition times: (a) 5 seconds (b) 1 minute. Both spectra were acquired using a 3 keV beam energy.

5.2.4 Automated SEM and EDX particle analysis

By utilising the "particle feature sizing" function in the JEOL-7100F SEM with the Thermo Scientific Noran System Seven, it is possible to perform automated EDX analysis of thousands of inclusions spread across the sample. This software was designed to aid in the investigation of gunshot residue. However, it can be used to search and analyse inclusions in a metal matrix. In beryllium the inclusions all appear bright compared to the surrounding matrix as the yield of backscattered electrons is much higher than the beryllium matrix. This enables the software to distinguish the particles as isolated regions in the surface.

To perform this analysis: a high resolution image of the sample surface is collected, which is typically 2048² or 4096² pixels. A contrast thresholding is then performed on the secondary electron image, allowing the identification of the brighter inclusions from the grey, beryllium background in the image. An example of this is shown in Figure 5.9. Here, the inclusions that will be analysed have all been marked in red by the software. At this point a filter can be applied, the filter allows the user to exclude any inclusions smaller than a certain number of pixels so as not to waste time trying to perform EDX on a single white pixel, which could correspond to noise in the image.
After thresholding the analysis details are chosen. These allow the user to: select the length of time to collect x-rays from each inclusion, add a chemical filter (e.g. discard data that does not contain Fe or Al), add a size filter (e.g. discard inclusions smaller than 50 nm), perform longer analysis on inclusions with a certain chemistry or set a termination point to stop the program after a set number of particles have been analysed. A typical live time for the analysis is 5 seconds for each area of interest. With the 30 mm² SDD fitted to the JEOL 7100F microscope this still enables max peak counts in excess of 20,000 for some inclusion types. The short live times are used to acquire the largest data set possible. Extended acquisitions allow the software to find an inclusion of particular interest, such as an AlFeBe₄ and acquire a longer live time spectrum, dramatically improving the signal to noise.

After applying the selected filters the desired area over which automated analysis is required is selected either as a single SEM FOV, a line or as a grid. In the line and grid analysis, a magnification is selected as well as the desired start and end points for the line or the four corners for the grid and the system will automatically divide the area into the selected number of frames to perform the analysis. The analysis then proceeds with: an SEM image being acquired, image thresholding, particle selection, EDX of each particle in the image, move to next position and repeat. The acquisition continues until the entire area has been acquired or it is stopped by the user.

Beryllium was not included as part of the quantification from these inclusions as a consequence of the problems quantifying beryllium, in addition to the very short acquisition times for automated EDX. Therefore, the quantification is best used as a guide to the ratios between other elements in the inclusion. The omission of beryllium from quantification is not expected to have a substantial effect on the reliability of the quantification of the other elements as the ZAF correction will not be significantly influenced by such a light element. Prior to the use of this function a manual analysis of ~400 inclusions was undertaken. The results of which are shown in Table 5.3.
Table 5.3 Results from a manual EDX analysis on 388 inclusions

<table>
<thead>
<tr>
<th>Composition</th>
<th>Number of inclusions</th>
<th>Percentage of total (%)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al + Fe</td>
<td>90</td>
<td>23</td>
<td>Al, Fe similar at.%</td>
</tr>
<tr>
<td>O rich</td>
<td>80</td>
<td>21</td>
<td>O rich + Be rich, trace levels other elements</td>
</tr>
<tr>
<td>C rich</td>
<td>40</td>
<td>10</td>
<td>C at.% &gt;30 trace other elements</td>
</tr>
<tr>
<td>Cd + Zr</td>
<td>17</td>
<td>4</td>
<td>O, C and Be containing trace other elements</td>
</tr>
<tr>
<td>Ti + Si</td>
<td>46</td>
<td>12</td>
<td>Ti$_3$Si / Ti$_3$Si</td>
</tr>
<tr>
<td>Si</td>
<td>29</td>
<td>7</td>
<td>Si, little or no Be</td>
</tr>
<tr>
<td>Al + O</td>
<td>46</td>
<td>12</td>
<td>Al$_2$O$_3$</td>
</tr>
<tr>
<td>N</td>
<td>3</td>
<td>1</td>
<td>Be$_3$N$_2$</td>
</tr>
<tr>
<td>Other Mixed</td>
<td>37</td>
<td>10</td>
<td>Mix of trace levels of transitions metals</td>
</tr>
</tbody>
</table>

Automated analysis provided an analysed area of 0.5625 mm$^2$. A total of 1883 inclusions were analysed from a sample that had been UV-Ozone cleaned. The results are shown in Table 5.4. The combination of cleaning and low analysis times avoids the problem of carbon deposition on the surface, which would increase the apparent concentration of carbon within the inclusion. The most noticeable difference between the manual and automated analyses is the decline in the percentage of carbon rich and the aluminium oxide inclusions. The reduction in the carbon rich inclusions is explained by the increased cleanliness of the sample surface and the shorter spectral acquisition time. The fall in the number of aluminium oxide inclusions is likely a consequence of the removal of bias in the automated analysis. A manual analysis will have been affected by selecting the larger, easier to spot, inclusions while the automated analysis will pick up on any inclusion within the size range of a few pixels. Both the automated and manual analyses were performed on the same sample.

The inclusion types can be characterised using the ratio of elements present in an intermetallic, as is the case with aluminium alloys [98]. The AlFe type intermetallics were characterised by having an Al:Fe ratio of between 0.7 and 1.3. The beryllium oxide, beryllium carbide, beryllium nitride and elemental silicon inclusions were characterised using oxygen concentration of > 80 at.%, carbon concentration of > 30 at.%, nitrogen concentration > 80 at.% and silicon concentration > 80 at.%. The Cd/Zr inclusions were characterised by Cd or Zr > 10 at.%. The Ti$_3$Si inclusions were characterised by having a Ti:Si ratio of between 1.5-3.5. The Al$_2$O$_3$ inclusions were characterised by an Al:O ratio of between 0.5-1.

Table 5.4 Results from automated EDX analysis of 1883 inclusions. *mixed contained varying concentrations of transitional metal element: Al, Si, Ti, Mn, Cr, Fe, Ni, Cu, Zr and Cd

<table>
<thead>
<tr>
<th>Composition</th>
<th>Number of inclusions</th>
<th>Percentage of total (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlFeBe$_3$</td>
<td>570</td>
<td>30</td>
</tr>
<tr>
<td>BeO</td>
<td>609</td>
<td>32</td>
</tr>
<tr>
<td>Be$_2$C</td>
<td>4</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Cd + Zr</td>
<td>2</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Ti$_3$Si</td>
<td>291</td>
<td>15</td>
</tr>
<tr>
<td>Elemental Si</td>
<td>27</td>
<td>1.5</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>54</td>
<td>3</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td>Be$_3$N$_2$</td>
<td>2</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Other mixed*</td>
<td>304</td>
<td>16</td>
</tr>
</tbody>
</table>
All of the data shown in Table 5.4 was combined with the size of the inclusions, as found by the feature sizing software and a histogram was produced. Figure 5.10 shows the size distributions for all of the intermetallic types identified by the automated EDX analysis of 1883 inclusions. The histogram has been shortened to only show the smallest inclusions that are < 20 μm². The largest inclusions present in beryllium were omitted for clarity. The largest inclusions were all Al₂O₃ with traces of other elements. These ceramic particles ranged in size from 1-100 μm² and are visible when examining the surface of the sample with RLM.

![Histogram of the size distribution with composition of the inclusions in beryllium following EDX of 1883 inclusions.](image)

In addition to the histogram for all inclusion types, another was plotted for the inclusion of most relevance to the current work, the AlFeBe₄ precipitate. This is shown in Figure 5.11. It shows how all of the precipitates identified by EDX are smaller than 10 μm² and > 90% are smaller than 5 μm². The data indicates that finding the largest possible AlFeBe₄ precipitates for the study of corrosion processes would require searching a large area of the sample surface.

![Histogram of the sizes of AlFeBe₄ type intermetallics from the data set of 1883 inclusions.](image)
5.3 Wavelength dispersive x-ray spectroscopy

5.3.1 Improved sensitivity

The enhanced sensitivity for the light elements in WDX has been utilised to analyse beryllium. To highlight the enhanced sensitivity three spectra, each collected in 1 second from a beryllium surface are overlaid in Figure 5.12. These show a WDX spectrum (blue), an EDX spectrum collected with a long time constant (red) and an EDX spectrum collected using a short time constant (black). The increase in the peak sensitivity of the Be Kα is evident. Using WDX it is possible to achieve an x-ray storage rate exceeding 6350 counts s⁻¹ but if EDX is used, it is only possible to achieve 450 counts s⁻¹ at the same probe current. EDX generates a maximum x-ray yield of 4 counts s⁻¹ nA⁻¹, with the lowest time constant and 1 counts s⁻¹ nA⁻¹, with the highest time constant. While in WDX the maximum x-ray yield is 59 counts s⁻¹ nA⁻¹.

![Graph showing EDX and WDX spectra collected from beryllium in 1 second.](image)

5.3.2 Second phase particles analysis

WDX allows the unambiguous identification of the elements present in an inclusion when using a low beam energy. Based upon the results of the extensive automated EDX analysis of inclusions, the elements present in the second phase particles were found to be: Be, C, N, O, Al, Si, Ti, Cr, Mn, Fe, Zr, Ni, Cu and Cd, at various concentrations. All of these have x-ray lines of a suitable energy such that a 3-5 keV beam energy provides a significant excitation energy for analysis, while ensuring the interaction volume does not extend too far beyond the particle and into the matrix.

Shown in Figure 5.13 (a-c) are the EDX spectra collected from three inclusions at a beam energy of 3 keV. Overlaid on them are the WDX spectra for the Be Kα peak (red). The Be Kα in WDX was collected over a ~20 eV energy range. They illustrate how WDX can be utilised to confirm the presence of beryllium in an inclusion.
The increased sensitivity of WDX over EDX is again highlighted in the line scans collected from an AlFeBe₄ precipitate. Figure 5.14 shows the SEM micrograph of the inclusion of interest. The image quality is poor as it was collected with a high probe current ~100 nA. The probe current was set as high as possible so as to maximise the x-ray yield for WDX. A line scan with 50 points was performed along the long axis of the inclusion, over a length of ~6 μm, at a beam energy of 3 keV. EDX lines for beryllium, oxygen, iron and aluminium are shown as well as a WDX line scan for beryllium. The standalone line scan images are shown in Figure 5.15.
Chapter 5  The Electron and X-ray Spectra of Beryllium

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5.4 X-ray photoelectron spectroscopy

5.4.1 Beryllium metal

While awaiting samples of beryllium from the sponsor company and to become more knowledgeable about surface analysis, XPS was performed on a sample of S-65 beryllium purchased from Goodfellow Cambridge. Figure 5.16 shows a survey spectrum acquired from the sample after argon ion etching. It was analysed using a 400 μm spot size, a pass energy of 300 eV and a step size of 0.5 eV. The spectrum was charge corrected to the C 1s peak at 285.0 eV. Impurity elements present in the beryllium are observed, these include copper, nickel and fluorine. The fluorine is present as a result of the production of beryllium metal utilising a reduction of beryllium fluoride with magnesium. Argon is present as a result of ion implantation during the sputtering process. A particularly small peak at ~1383 eV (103 eV on a kinetic energy scale) is observed, this peak is the beryllium Auger transition.

Figure 5.15 EDX line scan and WDX beryllium line scan from an AlFeBe₄ precipitate.

The line scans show how the EDX beryllium signal (red) decreases slightly when moving from the bulk beryllium onto the precipitate, compared to the WDX signal (black) which changes significantly. The changes in counts are ~570 to 270 in EDX and 2970 to 860 in WDX. A significant proportion of the counts for the EDX beryllium signal will also be background intensity, as can be seen from the line scans for aluminium and iron (blue and yellow respectively). Their counts rates do not fall to zero despite their low concentration in the bulk beryllium distant from the inclusion, this is a consequence of the x-ray background which is quite large at the Al Kα and Fe Lα regions of the spectrum.
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A clean surface is required in order to observe the beryllium Auger transition because, being only ~100 eV in kinetic energy, it is easily attenuated by a carbon over layer. The carbon contamination thickness was calculated as ~0.2 nm (carbon ~10 at.%), while the depth of analysis for the Be KLL transition was calculated as ~0.9 nm, in carbon. The attenuation length, in beryllium, of the higher kinetic energy Be 1s electrons is ~5x greater than the low energy Be KLL electrons, with lengths of ~3.1 nm and 0.6 nm, respectively.

The Be 1s high resolution spectrum, shown in Figure 5.17, was peak fitted with metal and oxide components in addition to a small carbonate peak. A corresponding carbonate peak was also observed in the high resolution C 1s spectrum. Carbonates are readily formed on the surface of alkali and alkali earth metals when they are exposed to air. The metal peak was located at 110.5 eV, the oxide at 113.5 eV and the carbonate at 114.7 eV.

The high resolution spectrum of the beryllium Auger transition is shown in Figure 5.18. Components corresponding to the metal and the oxide are observed. Two components to the lower kinetic energy side of the primary metal and oxide peaks are also observed, these are the additional components of the oxide Auger structure and are discussed in a later section. The peak components were recorded at 102.5 eV, 94.0 eV, 87.0 eV and 78.0 eV. It is evident, upon examination of the Be 1s and the Auger transition, that the peak
separation between oxide and metal components is larger for the Auger peaks than the photoelectron peaks, ~9.5 eV and 3 eV respectively.

Figure 5.18 High resolution beryllium Auger spectrum from the air-exposed metal surface.

5.4.2 Beryllium oxide

In addition to the metal, a sample of beryllium oxide was also purchased from Goodfellow Cambridge. This was analysed to gain a further understanding of beryllium compounds and to learn about the use of charge compensation in photoelectron spectroscopy. Figure 5.19 shows a survey spectrum acquired from the beryllium oxide sample. It was analysed using the same settings as used for the metal with the additional use of an electron flood gun with argon bleed, for charge neutralisation. The spectrum was acquired prior to argon ion etching, in the as-received form. A significant amount of contamination was observed on the beryllium surface, these contaminate elements were: magnesium, sodium, chlorine and silicon. Unlike on the metal sample, the beryllium Auger transition at high kinetic energy is not observed, showing that the contamination layer was sufficiently thick to attenuate the Auger electrons. The carbon contamination thickness was calculated as ~0.8 nm (carbon ~33 at.%) and the depth of analysis for the Be KVV was calculated as ~0.9 nm in carbon, indicating that the Auger electrons would be almost fully attenuated by the carbon contamination.

Figure 5.19 Survey spectrum from beryllium oxide.

High resolution spectra were collected, in addition to the survey spectrum, following charge neutralisation. Figure 5.20 shows the high resolution Be 1s spectrum from beryllium oxide. The Be 1s had a binding energy
of 113.5 eV, which matched that observed on the native oxide. A small amount of peak broadening is observed compared to the oxide peak from the native oxide. This probably indicates a small degree of charging at the surface or perhaps vertical differential charging. The FWHM was recorded as 1.9 and 2.4 eV for the native oxide and bulk oxide BeO peaks, respectively.

![Figure 5.20 High resolution Be 1s spectrum from beryllium oxide.](image1)

The Be $KVV$ was not initially observed on the oxide as the carbon contamination layer was so thick. Figure 5.21 shows the high resolution spectrum of the Be $KLL$ from the oxide which was obtained following substantial argon ion etching. The metal component that was observed for the native oxide on beryllium is no longer observed. Two additional components to the lower kinetic energy side of the primary transition are also observed. The transitions were recorded at 93.3 eV, 86.7 eV and 77.7 eV. Significant argon ion etching was required in order to acquire the spectrum, as a consequence of the thick carbon contamination layer and the considerable roughness of the surface.

![Figure 5.21 High resolution Be $KVV$ Auger transition from beryllium oxide.](image2)

### 5.5 Auger electron spectroscopy

#### 5.5.1 Background

As previously discussed in Chapter 2, beryllium and the native oxide, have been studied using AES. The current published literature displays the Auger data in differential mode, making comparisons to modern data more difficult, as it is now usual to display a spectrum in the direct form. The beryllium carbide and
beryllium nitride spectra were recorded from inclusions present in beryllium samples of known provenance provided by the sponsor. These inclusions were too small to analyse by XPS but could be analysed by AES. Beryllium nitride and beryllium metal are conductive and so could be analysed in the usual manner. However, beryllium oxide and beryllium carbide are insulators and so required the analytical methodology to be developed.

No spectra from bulk beryllium oxide are available in the literature, the spectra to date are those collected from a thick native oxide grown during oxidation of metallic beryllium. These spectra were collected with CMA with a maximum energy resolution of 0.5%. However, because the kinetic energy of the beryllium Auger transition is so low, this resolution is suitable for the identification of chemical states. A resolution of 0.5% in CRR mode corresponds to a CAE of 25 eV, at this kinetic energy. This is sufficient to resolve chemical states. As such, whilst the energy resolution of the HSA used in this project was much greater than the older CMAs, changing from 0.5% to 0.05% resolution, showed no additional spectral information. Therefore, all the high resolution spectra shown in this section were collected with a CRR of 4 and a resolution of 0.5%.

### 5.5.2 Beryllium metal

To investigate the beryllium Auger transition a piece of polished beryllium was analysed in a number of ways to provide different pieces of spectral and sample information. The survey spectrum collected from the as-received surface of beryllium is shown in Figure 5.22. The Be KLL, C KLL and O KLL are the only Auger transitions observed. The C KLL was produced by a small amount of carbon contamination and not beryllium carbide, which would show a characteristic carbide peak shape in the C KLL.

![Figure 5.22 Survey spectrum from as-received beryllium metal.](image)

Analysis of the native surface revealed the presence of a number of transitions within the kinetic energy range of the Be KLL. The transitions from beryllium metal and beryllium oxide were observed in the high resolution spectrum, as shown in Figure 5.23. The depth of analysis for the Be KLL electrons was calculated as ~1.1 nm, in beryllium. The Auger transitions are consistent with that observed in the XAES spectrum shown in Figure 5.18. The peaks were recorded with kinetic energies of 103.0 eV, 93.7 eV, 87.0 eV, 78.0 eV and 67.5 eV. A retard ratio of 4 was used in the acquisition of the spectrum, corresponding to a CAE of ~25 eV. This provided a higher spectral resolution than the XAES spectrum which was collected with a CAE of...
200 eV. Considering the large difference in the pass energies used to collect the Auger transitions there was little change in peak width. Therefore, it can be concluded that the spectral resolution is limited by the Auger peak width and not analyser resolution.

By scribing the sample surface in vacuum, it was possible to isolate the metallic beryllium surface. This enabled a spectrum to be acquired with only the metal peak component. Figure 5.24 shows the survey spectrum collected from the scribed region. A small trace of oxygen is observed in the survey spectrum, this oxygen was the result of gradual oxidation of the exposed metal in the vacuum because beryllium is a particularly good oxygen getter. The KLL region was collected prior to the survey spectrum, decreasing the amount of oxidation which would interfere with the metallic Auger component in the high resolution spectrum.

Figure 5.25 shows the high resolution beryllium Auger region from the centre of the scribed region. A strong metallic beryllium Auger transition is observed at 102.5 eV, the beryllium oxide Auger peak at ~93.7 eV is not observed showing complete removal of the surface oxide. The feature to the lower kinetic energy side of the main transition is a bulk plasmon loss peak. The beryllium atom has four electrons in the configuration 1s^22s^2 as such the Auger peak consists of the KL1L1 Auger transition and this is formally denoted as the Be KLL Auger transition.
To isolate the oxide Auger components of the native oxide on beryllium, the ability to tilt the sample stage within the MICROLAB 350 was utilised. The tilting stage allows angle resolved AES to be performed. Unlike parallel angle resolved electron spectroscopy the spot size at the sample surface increases with the tilt angle but this was not an issue in this analysis. By tilting the sample away from the analyser by 15°, the Auger electron take off angle relative to the sample normal was increased from 50° to 65°. The result was a reduction in the average depth of analysis from 1.1 nm to 0.7 nm for the Be KLL, in beryllium. In doing so the metallic component was entirely removed from the beryllium Auger region, as shown in Figure 5.26, and the AES spectrum is consistent with the XAES spectrum from beryllium oxide. Unlike the spectrum collected from the metal surface the spectrum from the oxide showed four transitions. These were at kinetic energies of: 93.7 eV, 87.0 eV, 78.0 eV and 67.5 eV. Little sample charging was expected in this spectrum as the thin surface oxide is fully penetrated by the exciting primary electron beam. Therefore, the majority of the electrons from the primary beam were grounded. Figure 5.27 shows the survey spectrum collected from the titled beryllium surface. The Be KVV, C KLL and O KLL transitions are observed. The carbon was present as contamination.
5.5.3 Beryllium oxide and the analysis setup for insulating samples

Analysis of beryllium oxide proved to be particularly challenging. The analysis of insulating samples in XPS is routinely carried out utilising an electron flood gun with an argon bleed. However, the Auger analysis of insulators is much less routine. A number of methods described in the literature were investigated to try and produce acceptable results [99].

The first attempt involved wrapping the sample in aluminium foil and analysing the surface through a small pinhole. The intended effect of which was to cause the excess electrons to be grounded through the aluminium foil. This was unsuccessful. A second attempt was to flood the surface with low energy argon ions (<50 eV) from the EX05 argon ion gun. The use of low beam energies of <5 keV were also tried but to no effect on the horizontal surface. The use of a conductive silver paint was also investigated to try and create a conductive pathway around a small region to ground the analysed area but this was also unsuccessful.

The successful analysis of the bulk oxide was eventually achieved by tilting the sample to almost grazing excitation. The sample was held at 80° from horizontal providing an excitation angle of 10°. By tilting to this angle the primary electron beam strikes the surface at a grazing angle and fewer electrons interact with the substrate. As well as sample tilting, the beam energy was reduced to 2.5 keV. This reduces the interaction volume within the material, reducing the secondary electron cascade produced by the beam, helping to minimise sample charging. These effects are highlighted in Figure 5.28. This shows the sample orientation in the MICROLAB 350, overlaid with a Monte-Carlo simulation of the electron cascade from a 2.5 keV primary electron beam. It can be observed that a significant proportion of the cascade is scattered outside of the substrate, reducing the number of secondary electrons within the substrate which contribute to charging. If the simulation is repeated for a 10 keV beam the cascade is approximately an order of magnitude greater in size. Additionally, if no sample tilt is applied the entire interaction volume exists within the substrate. If charging is still observed, after these steps, it is possible to lower the beam energy further but to ensure high excitation cross sections beam energies of 3-5x the kinetic energy of the peaks of interest are desired in AES.
If the previously described charge control procedures are not followed, no useful information can be extracted from the spectrum collected from an insulating surface, this is shown in Figure 5.31. This shows the effect on the survey spectrum collected from an insulating sample surface without charge control procedures.

Close examination of the survey spectra collected from beryllium oxide and beryllium carbide, which are insulators, show an improved signal to noise compared to the spectra collected from beryllium and beryllium nitride. This is a useful consequence of the experimental setup for insulating samples. By tilting the sample, the electron beam spot is extended over a much larger area. Therefore, although the total flux of electrons hitting the sample remains constant, a much greater number of primary electrons generate Auger electrons that can escape the sample surface. By tilting the sample to 80° the expected spot size is ~240 nm.

In addition to the elongated spot there is another advantage provided by the methodology. The low beam energy used to analyse insulating samples causes the electron cascade to be generated closer to the surface. As such, more of the secondary electrons and backscattered electrons are able to excite Auger electrons that can escape the surface. For beryllium and the beryllium nitride inclusions, which are conductors that were
analysed with a 10 keV primary beam energy, the majority of the electron cascade is deep within the sample and so far fewer of the secondary and backscattered electrons excite Auger electrons that are able to escape the surface.

Figure 5.29 shows the survey spectrum collected from bulk beryllium oxide, using the experimental methodology described for insulating samples. It shows the Be KVV and O KLL Auger transitions as a well as a small C KLL from surface contamination. The signal to noise is superior to the survey spectrum collected from the native oxide shown in Figure 5.27, although the background is also significantly greater.

Figure 5.29 Survey spectrum from bulk beryllium oxide.

The kinetic energies of the peaks were charge corrected by ~4 eV to align them to the peaks observed in the beryllium metal native oxide layer, isolated by tilting the sample away from the analyser. The spectrum is consistent with that observed from the isolated native oxide and the beryllium oxide Auger transition observed in the photoelectron spectrum. The high resolution Be KVV spectrum, shown in Figure 5.30, shows all of the oxide peaks that were observed in the spectrum collected from the native oxide, as shown in Figure 5.26. The peak positions were recorded as: 93.7 eV, 87.3 eV, 78.0 eV and 67.5 eV, the same as were observed for the native oxide. Compared to the native oxide spectrum, which was free of sample charging, the peaks are slightly broader.

Figure 5.30 High resolution Be KVV spectrum from bulk beryllium oxide.
The metal Auger peak is labelled as a $KLL$ transition because it involves the $1s^22s^2$ electron configuration with the associated $KL_1L_1$ transition. The beryllium atom in beryllium oxide is in the configuration $1s^22s^0$. As such, the extra electrons required for the $KL_1L_1$ are not present in the $2s$ orbital. The electrons required to produce the Auger transition must therefore originate in the valence band or as a cross transition from the oxygen $L$ orbitals, so called “spectator states [100]. Therefore, it is incorrect to refer to the Auger peaks as $KLL$ transitions when they should be correctly labelled as $KVV$.

The energy of the various transitions can be calculated using the binding energies of the different electron orbitals that might be involved. Through the combination of the core binding energies, the valence band and the density of states it is possible to identify the four components of the oxide Auger transition. These components are the $KV_1V_1$, $KV_2V_1$, $KL_{i}(O)V_{1,2}$ and the $KL_{i}(O)L_{i}(O)$. $V_1$ and $V_2$ are the upper and lower maxima in the density of states from the valence band, respectively and $L_{i}(O)$ is the $2s$ electron from the oxygen atom to which the beryllium atom is bound. The experimentally derived peak positions from these transitions together with the actual observed transitions are shown in Table 5.5, the calculated values are derived from the literature and from peak positions in the XPS spectrum collected from beryllium oxide [100]. The binding used were: Be $1s$ 113.5 eV, O $2s$ 23.5 eV, $V_2$ 11.0 eV and $V_1$ 7.6 eV.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Calculated energy (eV)</th>
<th>Calculated energy (eV) adjusted*</th>
<th>Observed energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$KV_1V_1$</td>
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<td>95.5</td>
<td>93.7</td>
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<tr>
<td>$KV_2V_1$</td>
<td>94.9</td>
<td>93.1</td>
<td>87.3</td>
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<tr>
<td>$KV_2V_2$</td>
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<tr>
<td>$KL_{i}(O)V_1$</td>
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<td>81.0</td>
<td>78.0</td>
</tr>
<tr>
<td>$KL_{i}(O)V_2$</td>
<td>79.0</td>
<td>78.6</td>
<td></td>
</tr>
<tr>
<td>$KL_{i}(O)L_{i}(O)$</td>
<td>66.5</td>
<td>-</td>
<td>67.5</td>
</tr>
</tbody>
</table>

*adjusted values have used valence binding energies from boron nitride. 9.0 eV and 11.4 eV have been used for $V_1$ and $V_2$ [101].

The calculated values for the peak positions involving the spectator states from the O $2s$ orbital agree with the observed peak positions. However, those involving the calculated energies do not. The variance in the values is a result of not taking the core hole into account for the valence band binding energies. As shown in Chapter 2, the final electron involved in the Auger process does not have the same energy as the previous electron originating from the same orbital. The electrons energy will be greater because it feels the effect of the missing electron. The decrease in screening of the nucleus results in the Auger electron being emitted from an atom with an effective mass of $Z + 1$ [102,103]. As such, the calculated energies of the final valence band electrons $V_1$ and $V_2$ need to be adjusted as if they originate from a boron atom and not a beryllium atom. This would increase the energy of the emitted $V_1$ and $V_2$ electrons aligning the energy of the calculated energies closer to the observed energies as shown in the adjusted values in Table 5.5. The original literature describing the fine structure of the oxide Auger peak did not correct for the $Z + 1$ effect and so the published values had a greater disagreement to the adjusted values shown in the table.
5.5.4 Beryllium nitride

Beryllium nitride was isolated in the form of inclusions within the beryllium matrix, supplied by the sponsor. The beryllium nitride and carbide inclusions were identified as part of the automated analysis of inclusions in beryllium. The surface of the inclusions was lightly argon ion etched to remove a thin oxide layer. EDX and WDX analysis of the inclusions showed only beryllium and nitrogen to be present, as such it was assumed these inclusions were $\text{Be}_3\text{N}_2$. Figure 5.32 shows an SEM micrograph of three beryllium nitride inclusions which were analysed by AES. The survey spectrum, collected from the largest inclusion, is shown in Figure 5.33. It showed a small $\text{O KLL}$ peak and intense $\text{Be KVV}$ and $\text{N KLL}$ peaks. The $\text{O KLL}$ was the result of slight oxidation during analysis.

![Figure 5.32 SEM micrograph of three beryllium nitride second phase particles in beryllium.](image)

![Figure 5.33 Survey spectrum from a beryllium nitride inclusion.](image)

The beryllium nitride $\text{KVV}$ is similar to the beryllium oxide $\text{KVV}$. Three weaker transitions are observed in addition to the primary transition. A small peak is observed to the high kinetic energy side of the primary transitions, this may be the Be $\text{KLL}$ Auger transition which is a result of some x-ray fluorescence within the particle exciting Auger electrons from the surrounding metal matrix. As for the oxide Auger spectrum the transitions in the $\text{KVV}$ are $\text{KV}_1\text{V}_1$, $\text{KV}_2\text{V}_2$, $\text{KL}_{1}(\text{N})\text{V}_{1,2}$ and the $\text{KL}_{1}(\text{N})\text{L}_{1}(\text{N})$. $\text{V}_1$ and $\text{V}_2$ are the upper and lower maxima in the density of states from the valence band, respectively and $\text{L}_{1}(\text{N})$ is the 2s electron from the nitrogen atoms to which beryllium is bound.
The experimentally derived peak positions from these transitions together with the actual observed transitions are shown in Table 5.5, the calculated values are derived from the literature. The binding used were Be 1s 113.7 eV, N 2s 18.5 eV, V₂ 11.4 eV and V₁ 9.0 eV. Beryllium nitride is a less widely studied material compared to beryllium oxide and so the binding energies for the N 2s, V₂ and V₁ could not be found in the literature. A value for the N 1s in beryllium nitride was found as well as values for the N 1s and N 2s in boron nitride. The boron, being less electropositive, shows a shift of -0.9 eV compared to the N 1s peak from beryllium. For a rough approximation of the N 2s peak position in beryllium nitride this shift was applied to the 2s binding energy. The valence values have been used from boron nitride. Despite the use of boron nitride values for the valence band and the estimated value for the N 2s binding energy, the calculated energies agree well with the observed energies. The smaller energy differences between the lower kinetic energy peaks and the primary peak for the nitride, compared to the oxide, reflect the lower binding energy of the electrons in nitrogen compared to oxygen.

Table 6 Calculated and observed energies of peaks in the Be₃N₂ Auger transition

<table>
<thead>
<tr>
<th>Transition</th>
<th>Calculated energy (eV)</th>
<th>Observed energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KV₁V₁</td>
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<td>96.7</td>
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</tr>
<tr>
<td>KV₂V₂</td>
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</tr>
<tr>
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<td>85.3</td>
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<tr>
<td>K L₁(N) L₁(N)</td>
<td>76.7</td>
<td>78.1</td>
</tr>
</tbody>
</table>

*Boron nitride values for the valence binding energies as beryllium nitride data was not available.

5.5.5 Beryllium carbide

Beryllium carbide was also isolated in the form of inclusions within the beryllium matrix. Prior to analysis the surface was argon ion etched and scribed in vacuum to remove a thick oxide layer. EDX showed beryllium, carbon and trace amounts of nitrogen and oxygen. Figure 5.35 shows an SEM micrograph of a beryllium carbide second phase particle. The central bright region is the carbide particle which shows significant charging. Spectra from the carbide were collected using the same methodology, as previously described for the analysis of bulk beryllium oxide and other insulating samples.
The survey spectrum acquired from the particle is shown in Figure 5.36. It shows intense Be \textit{KLL} and C \textit{KLL} transitions together with weaker N \textit{KLL} and O \textit{KLL} Auger transitions. The nitrogen and oxygen are present as a result of impurities, as well as slight surface oxidation during analysis. A weak Ar \textit{LMM} transition is also observed on the loss tail of the carbon peak at \( \sim 215 \) eV. This was observed as a result of argon implanted during etching.

The high resolution C \textit{KLL} Auger transition, together with the differential spectrum are shown in Figure 5.37 (a + b). The carbon region also shows the weak Ar \textit{LMM} transition. The C \textit{KLL} shows the characteristic, series of three peaks revealing the presence of a carbide and not hydrocarbon contamination. The peak positions in the direct form were 269.0 eV, 257.8 eV and 251.0 eV. The peak positions in the differential form were: 277.0 eV, 259.2 eV and 252.7 eV. The peak positions in the differential spectrum as recorded at the peak minima.
The high resolution Be \( KLL \) Auger transition collected from the carbide is shown in Figure 5.38. The spectrum is strikingly similar to the metal spectrum and the primary peak position was recorded as 100.4 eV. Compared to the metal spectrum a slight reduction in the width of the transition is observed as well as a large reduction in the intensity of the plasmon loss peak, at \(-80\) eV, which is barely discernable. The appearance of the spectrum is unlike the nitride or the oxide and is almost identical to the metal Auger transition. This reveals the commonality in the bonding characteristics of beryllium metal and beryllium carbide which both display significant covalent bonding. The absence of the fine structure reveals that the beryllium Auger transition from the carbide does not contain spectator states or any evidence for ionic bonding character, as such the Auger peak has been labelled as a \( KLL \) transition.

5.6 Wagner chemical state plot for beryllium and beryllium compounds

By combining the data from the AES analysis with the previously described XPS data, it was possible to construct a Wagner chemical state plot for the modified Auger parameter for beryllium. The plot is shown in Figure 5.39. The data used to calculate the values in the plot are shown in Table 5.7. These were obtained from the previously presented spectra and from the literature in the case of the photoelectron peak positions for the nitride and carbide. These were required because the nitride and carbide inclusions were too small to obtain good quality photoelectron spectra from. The \( \text{Be}_2\text{C} \) and \( \text{Be}_2\text{N}_2 \) Be 1s values were referenced to
metallic beryllium at 110.5 eV and the Be 1s and BeO 1s values were referenced to carbon at 285.0 eV [104–107].

Figure 5.39 Wagner chemical state plot for beryllium and beryllium compounds.

Table 5.7 Auger and photoelectron peak positions for the beryllium compounds

<table>
<thead>
<tr>
<th>Material</th>
<th>Formula</th>
<th>Be $KLL$ (KE/eV)</th>
<th>Be 1s (BE/eV)</th>
<th>Be 1s (KE/eV)</th>
<th>Modified Auger parameter $\alpha^*$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beryllium</td>
<td>Be</td>
<td>103.0</td>
<td>110.5</td>
<td>1376.2</td>
<td>213.5</td>
</tr>
<tr>
<td>Beryllium carbide</td>
<td>Be$_2$C</td>
<td>100.4</td>
<td>111.3</td>
<td>1375.4</td>
<td>211.7</td>
</tr>
<tr>
<td>Beryllium nitride</td>
<td>Be$_3$N$_2$</td>
<td>96.7</td>
<td>113.7</td>
<td>1373.0</td>
<td>210.5</td>
</tr>
<tr>
<td>Beryllium oxide</td>
<td>BeO</td>
<td>93.7</td>
<td>113.5</td>
<td>1373.2</td>
<td>207.2</td>
</tr>
</tbody>
</table>

In addition to the Wagner chemical state plot, the shift in the kinetic energy with changing chemical state is highlighted in Figure 5.40. This shows the Auger transitions from beryllium metal, oxide, nitride and carbide, plotted on the same axis.

Figure 5.40 Overlaid spectra of the $KLL$ Auger transitions from four chemical states of beryllium.
5.7 Conclusions

Following the automated analysis of ~2000 inclusions little evidence for carbide inclusions was found on a UV-Ozone cleaned surface, in a SEM with good vacuum. The most common types of inclusion were BeO particles and AlFeBe₄ precipitates. The largest inclusions were all of the Al₂O₃ type. Additionally, no iron beryllides were identified as iron was always found to be associated with aluminium. Titanium was also found to always be associated with silicon and never present by itself.

WDX analysis using a low beam energy proved useful in isolating the inclusions from the beryllium matrix, enabling the confirmation of beryllium within the inclusion.

Although beryllium and beryllium compounds posed significant challenges in their analysis, high quality spectra from the metal, oxide, nitride and carbide were obtained. Various methods were employed to obtain high quality spectra and of those tested the combination of a low primary beam energy and sample tilting was found to work well for insulating samples.

Upon completion of the XPS and AES investigations on the beryllium compounds it was possible to construct a Wagner chemical state plot for beryllium. This will enable other researchers working with beryllium compounds to accurately assess the chemical state of species in their system independently of sample charging. It is hoped that this plot will be expanded by others in future.

Following completion of the x-ray and electron spectroscopic analysis of beryllium and the wide range of second phase particles present in the beryllium samples, the corrosion of beryllium, paying particular attention to the role of the second phase particles will be examined in the next chapter.
Chapter 6 - Corrosion of Beryllium

6.1 Introduction

6.1.1 Handling beryllium

A series of general guidelines were established, prior to the corrosion experimental work, in order to minimise the risk of exposure to beryllium, ensure good chemical laboratory practice and keep beryllium samples secure. Following acceptance of the beryllium samples from AWE they were stored in multiple, sealed, plastic bags with a desiccant in a safe. Access was limited to specific individuals and samples could only be removed after signing a log book. In the day to day experimental handling of beryllium for microscopy or spectroscopy prior to corrosion the samples were kept in the laboratory in a vacuum desiccator, placed in a bag and wrapped in aluminium foil. Moving the samples from one instrument to another was performed by keeping the samples wrapped in foil inside a zip-lock plastic bag. The sample was only removed once at the instrument and ready to place it directly inside.

The beryllium samples were handled and manipulated using plastic tweezers and the use of clips and screws to hold the sample in place was minimised to avoid damaging the beryllium and generating small particulates. After completion of the corrosion investigation the corroded beryllium was wrapped in aluminium foil and then double bagged in sealed plastic bags before being removed from the glovebox and returned to storage or to AWE for disposal.

Within the glovebox a number of additional measures were taken to avoid unnecessary release of beryllium particulates. The solid waste from the experiment including: tissues and gloves were placed into a labelled, sealable plastic bottle. The liquid waste from the test solution and rinse water was added to a separate labelled plastic bottle. These were both marked as toxic and as possibly containing beryllium. The bottles were double bagged prior to removal from the glovebox for disposal as hazardous waste.

6.1.2 Containment of beryllium during corrosion

The original project outline established by the University and AWE designated the requirement for the safe containment of beryllium particulates that could be generated during a corrosion investigation. Possible exposure of these particles would be minimised by performing all of the corrosion steps within a glovebag. This would then be connected to the entry lock of the MICROLAB 350, the glovebag is shown in Figure 6.1.
Following corrosion studies of aluminium using the glovebag it became apparent that it was not suitable for the intricate manipulation of the samples that the work required. The one-size gloves proved to be too large and the plastic material too slippery to grip samples and tools. To combat this problem the internal gloves were removed and replaced with thick neoprene laboratory gloves sealed to the arms using a rubber o-ring and adhesive tape. The modified glovebag was deemed to be inappropriate from a health and safety perspective as the original integrity and containment environment had been breached. After rejecting the glovebag solution, a suitable replacement was sought. Figure 6.2 shows the replacement equipment, a custom made soft-sided glovebox. This contained high-efficiency particulate arrestance (HEPA) filters on the air in and air out ports, internal quick change nitrile laboratory gloves, plastic base trays, an entry lock chamber and a bag out port.

The entry lock was included to enable the loading and unloading of equipment required for the corrosion investigation without the need to breach the integrity of the primary chamber. HEPA filters were added as standard but would allow the box to be operated at positive or negative pressure, if required. The quick change nitrile gloves dramatically improved dexterity when using the glovebox. The plastic base trays were added to provide a hard working surface to avoid possible damage to the bottom of the plastic and to contain any spills of rinse water or corrosive solution. The bag out port contained a length of flexible plastic lining.
that was connected to the glovebox with two rubber o-rings, the flexible plastic was then attached to the entry lock using a rubber o-ring and a cable tie. The glovebox was used for all of the beryllium corrosion.

### 6.2 Marking intermetallics

The production of beryllium metal utilises hot pressing of beryllium powder. This results in a random distribution of second phase particles along the grain boundaries in the finished metal. Figure 6.3 shows an RLM image highlighting the distribution of the particles in the metal surface. It was therefore, not possible to utilise the same method of marking the intermetallics that was previously used for the aluminium corrosion investigation in Chapter 4.

![RLM image of the beryllium surface, the black points are the second phase particles.](image)

In order to reliably relocate the same intermetallics a large grid of Vickers microhardness indents was generated. This grid consisted of 21 x 26 indents to produce 500 unique squares each approximately the same size. The grid is shown in Figure 6.4. It covered a 3 mm² region of the surface and each of the small squares was ~85 x 85 µm. A large indent was placed at the edge of the grid to ensure the sample could be placed in the correct orientation for analysis.

A load of 20 g was applied for 10 seconds to produce each indent. After an indent was made the sample was moved and the next indent was made. The grid was not completely square because of the difficulty in aligning the indents and measuring the spacing by hand. The large indent in the top right corner of Figure 6.4 required a load of 100 g for 10 seconds. The minimum loads to produce suitable microhardness indents were used. This was to minimise their effect of the corrosion process associated with the nearby second phase particles and to minimise the risk of generating beryllium particulates outside of the glovebox. The 20 g load was the lowest setting on the indentor that still enabled the indents to be readily observed in the SEM.
The grid allowed the repeated analysis of particles in the same geometry. The small squares were numbered sequentially from left to right and top to bottom such that the first square in the top left is “1” and the final square in the bottom right is “500”. Locating the second phase particles was then accomplished by counting the number of grids along and down within the SEM FOV.

To further investigate the second phase particles present within this grid, the automated EDX analysis that was previously described in Chapter 5 was performed. Following the analysis, a table was produced that listed each of the small squares with the number of particles with their size and their composition. The largest particles, with compositions of interest, were selected from the table for further investigation.

### 6.3 Experimental

A set of 8 x 8 mm samples of beryllium S-65 billet were wet ground with 600, 1200, 2500 and 4000 grit silicon carbide papers and then polished to a 1 μm finish at AWE. These were then ultrasonically cleaned using acetone and rinsed with DDI water. Samples were transported to the University tripled bagged in air tight plastic bags with an added desiccant. Samples were stored in a safe until required and transferred to the laboratory as required where they were wrapped in aluminium foil and stored in a dessicator.

A 0.1 M, pH 7 solution of sodium chloride was prepared from analytical grade NaCl and DDI water. The metallic specimen was UV-Ozone cleaned using a Hitachi Zone Cleaner for 5 minutes at 133 mbar and a working distance of 3 mm to remove carbonaceous contamination from the surface. The sample was then analysed using SEM, AES and EDX.

The sample was then immersed in the NaCl solution for 15 minutes. Following immersion, the specimen was rinsed with DDI water and dried on lint free tissue. The sample was then loaded into the entry lock, which was evacuated for 1 hour before the sample was transferred to the analysis chamber, where it was then analysed by AES and EDX. AES was always performed prior to EDX to minimise level of carbon in AES spectra. The analysis was repeated after 45 minutes, 2, 4, 8, 16, 32, 64 and 128 hours cumulative immersion in the chloride solution. At each time period the same intermetallics were analysed in the same geometry.
Attention was paid to align the SEM field of view (FOV) to ensure that the analysis positions were as constant as reasonably possible.

The investigation was performed using a Thermo Scientific MICROLAB 350 scanning Auger microscope fitted with an integral Thermo Scientific EDX detector. A primary electron beam energy of 10 keV was used for the acquisition of point Auger spectra, EDX spectra and SAM maps. The sample current was measured as 10 nA. A gun aperture of 150 μm was used to resulting in a spatial resolution of ~20 nm in the AES mode operation.

Auger survey spectra were recorded with an energy range of 50-1800 eV and a retard ratio of 4. The peaks recorded in the high resolution AES spectra and the SAM maps used various retard ratios, from 0.5-10, in order to collect chemical information in the AES spectra and maximise peak intensity in the SAM maps. 256 × 2 pixel SAM maps and 512 × 2 pixel EDX maps were acquired with acquisition times of ~14 hours and ~5 hours respectively.

6.4 Results

6.4.1 General results and observations

Initial analysis of the intermetallics was performed using the JEOL-7100F SEM. This microscope was used because of the superior imaging performance of the JEOL compared to the MICROLAB. The higher probe currents combined with the silicon drift detector EDX detector enabled the acquisition of EDX maps with significantly more counts per pixel and for this reason the phase maps for the intermetallics were generated from this EDX data and not that collected using the MICROLAB 350.

Following marking of the intermetallics, each was analysed using EDX. Additionally, an EDX spectrum was acquired from a 25 mm² area of the surface, to determine the average bulk composition of the metal. The quantification results from the EDX are shown in Table 6.1. Also shown are the areas of the inclusions which were measured from the SEM micrographs using ImageJ software [94].

Table 6.1 Compositions and areas of the intermetallics of interest, ND = not detected, - = omitted from quantification

<table>
<thead>
<tr>
<th>Intermetallic</th>
<th>Area (μm²)</th>
<th>Composition from EDX (at.% normalised)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Be</td>
</tr>
<tr>
<td>1</td>
<td>7.0</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>7.3</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>12.9</td>
<td>-</td>
</tr>
<tr>
<td>4 Al type</td>
<td>100.1</td>
<td>-</td>
</tr>
<tr>
<td>4 Fe type</td>
<td>4.6+7.4</td>
<td>-</td>
</tr>
<tr>
<td>5 Si half</td>
<td>2.1</td>
<td>-</td>
</tr>
<tr>
<td>5 Fe half</td>
<td>1.5</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>3.0</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>6.2</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>240</td>
<td>-</td>
</tr>
<tr>
<td>Additional 9</td>
<td>472</td>
<td>-</td>
</tr>
<tr>
<td>Bulk</td>
<td>61.3</td>
<td>1.0</td>
</tr>
</tbody>
</table>

The expected composition for S-65 beryllium is 99.2 at.% Be, 0.9% BeO, 0.05% Al, 0.08% Fe, 0.09% C, 0.01% Mg, 0.045% Si and 0.045% other. The EDX results reveal the problem with quantification of low
atomic mass elements in x-ray spectroscopy, which was discussed in Chapter 5. If quantification was more reliable the composition would more closely match that obtained by the chemical analysis of S-65 beryllium.

Following the acquisition of the initial SAM map, mapping was repeated when a change was observed in the point spectra at a specific time. If no change was observed in either the AES point spectra or EDX spectra then no mapping was performed with either technique to focus more analytical time on the intermetallics that were active. However, SEM micrographs were collected after each immersion stage. For these four inclusions EDX and AES point spectra are shown in the following sections for times 0, 15 min, 4 hours, 16 hours and 32 hours. These were selected to show if there was an immediate change or if there was a longer term change to the particles.

After 32 hours of immersion the analysis experimental was stopped. At this point the sample was transferred to the JEOL for some final high resolution SEM imaging, for this the sample was adhered to the sample holder using conductive silver paint. However, following this imaging, it was decided to continue the investigation further to 64 and 128 hours of immersion. EDX maps were acquired after 32 hours and 64 hours but only SEM images were acquired after 128 hours.

Throughout this Chapter EDX and AES spectra are stacked to save space and ensure that changes in the spectra as a function of time can be more clearly observed. They order of the immersion time changes in some figures to ensure the minimal peak overlap from intense peaks to increase clarity.

6.4.2 Intermetallic #1

6.4.2.1 Initial analysis

The first intermetallic chosen for further analysis is shown in Figure 6.5 (a). It was one of the largest AlFeBe₄ precipitates found by the automated EDX analysis routine. Examination of the micrograph shows a large central region of missing material. It is likely that part of the intermetallic had been removed from the surface by the polishing process. The large region of mechanical damage dramatically increases the surface area of the exposed intermetallic and provides a recess for possible crevice corrosion. The intermetallic was selected based upon it being a large particle but also because of the damaged region which was not observed on any of the other intermetallics investigated.

EDX phase analysis was performed on the x-ray maps collected from the SEM FOV. The resulting phase maps are shown in Figure 6.5. The analysis shows that the matrix (b) is homogeneous except for a few isolated oxide inclusions that decorate the grain boundaries surrounding the intermetallic (c). The main body of the intermetallic is homogeneous (d), but extends further subsurface than the outline observed in the SEM micrograph, particularly at the top of the intermetallic where the edges are poorly defined. The phase maps also reveal the presence of two small titanium-silicon intermetallics within the FOV (e).
Chapter 6

Corrosion of Beryllium

The EDX spectrum collected from the centre of the intermetallic is shown in Figure 6.6. The spectrum shows intense Al Kα and Fe Lα peaks, in addition to weaker Si Kα, Cr Kα and Mn Kα. Although there is a peak overlap between the Cr Kβ and the Mn Kα, the presence of manganese can be determined by the intensity of the Mn Kα peak. This is greater than the intensity of the Cr Kα peak and so if the peak was only from the Cr Kβ it would be significantly less intense. Weak C Kα and O Kα peaks are present from contamination and surface oxide. Quantification from the spectrum is shown in Table 6.2. It shows that the AlFeBe₄ precipitate contains an excess of aluminium compared to the ideal 1:1 aluminium to iron ratio. The intermetallic also contains a noticeable amount of silicon, chromium and manganese. Beryllium is omitted from the quantification.

![Figure 6.5 Phase analysis of the EDX maps collected using the JEOL SEM from Intermetallic #1: (a) SEM micrograph, (b) beryllium metal matrix, (c) BeO inclusions, (d) main AlFeBe₄ precipitate and (e) Ti-Si intermetallics.](image)

![Figure 6.6 EDX spectrum from the centre of Intermetallic #1.](image)

Table 6.2 Quantification from Intermetallic #1, normalised to 100%. Values with and without carbon and oxygen are shown, - designates an element omitted from quantification

<table>
<thead>
<tr>
<th>Composition</th>
<th>Be</th>
<th>C</th>
<th>O</th>
<th>Al</th>
<th>Si</th>
<th>Fe</th>
<th>Cr</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intermetallic (at.%)</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>53.3</td>
<td>6.4</td>
<td>32.8</td>
<td>3.2</td>
<td>4.3</td>
</tr>
<tr>
<td>Intermetallic (at.%)</td>
<td>0</td>
<td>1.9</td>
<td>15.4</td>
<td>43.2</td>
<td>5.1</td>
<td>28.2</td>
<td>2.6</td>
<td>3.5</td>
</tr>
</tbody>
</table>
In addition to the EDX spectrum, AES spectra were acquired from the same position in the centre of the intermetallic. They are shown in Figure 6.7. The survey spectrum (a) shows the surface predominately consists of beryllium, oxygen, iron and aluminium. A small amount of silicon and carbon contamination are also present. The oxide on the inclusion appears to be predominately beryllium oxide (c) with a possible trace of aluminium oxide (d). It is difficult to confirm the presence of aluminium in the oxide as the signal to noise in the high resolution spectrum is poor. It is also not possible to determine if iron is present in the oxide as the Fe \( LMM \) transitions do not show chemical state information. Silicon appears to be in elemental form (b).

![Figure 6.7 AES spectra from the centre of the intermetallic prior to corrosion. (a) Survey spectrum, (b) high resolution Si \( KLL \) spectrum, (c) high resolution beryllium Auger transition and (d) high resolution Al \( KLL \) spectrum.]

6.4.2.2 Analysis as a function of time

The SEM micrographs collected from the first intermetallic, after each immersion step, are shown in Figure 6.8 (a-j). They show the appearance of the intermetallic from time zero (a) to 128 hours (j). Little change is observed until 4 hours. The black areas of the surface are regions of carbon contamination. Between 4 hours (e) and 8 hours (f) of immersion a significant change is observed. Clusters of material encircle the inclusion and the material appears to be a constant distance from the centre of the particle. No material appears to have deposited onto the intermetallic itself. Between 4 hours and 8 hours of immersion the imaging magnification was reduced to ensure the entire region of interest was captured. After 16 hours of immersion (g) more material is observed to have deposited at the edge of the circle and again no material is observed on the intermetallic itself. After 32 hours (h) a significant change is observed. The halo of material has developed into a dome of corrosion products enveloping the matrix adjacent to the particle and the particle itself. The morphology of the dome is apparent in an SEM micrograph of the tilted sample in Figure 6.16. More
material is observed to deposit on and around the dome after 64 hours (i). Between 64 hours and 128 hours (h) little further change occurs.

Figure 6.8 SEM micrographs of Intermetallic #1 as a function of immersion time in NaCl. (a) Initial, (b) 15 min, (c) 45 min, (d) 2 hours, (e) 4 hours, (f) 8 hours, (g) 16 hours, (h) 32 hours, (i) 64 hours and (j) 128 hours.

EDX spectra were collected from the centre of the intermetallic and the local matrix or the corrosion products, once they had formed, following each immersion. The EDX spectra collected from the matrix are shown in Figure 6.9 and the spectra collected from the intermetallic are shown in Figure 6.10. Quantification was performed on the spectra collected from the intermetallic and the results are shown in Table 6.3. Quantification was not performed on the spectra collected from the matrix and the corrosion products...
because of the problems associated with beryllium quantification and so these spectra are presented as a qualitative view of the surface composition. The spectra collected from the matrix are consistent with bulk beryllium. Weak Be Kα and O Kα peaks are observed on a large Bremsstrahlung background. After 8 hours of immersion, the spectra were collected from the corrosion products. They show an intense O Kα peak as well as a weaker C Kα peak. As the immersion time increases, the concentration of chlorine associated with the products increases as shown by the increasing intensity of the Cl Kα peak.

Figure 6.9 EDX spectra collected from the matrix (0 and 15 min) and the corrosion products surrounding Intermetallic #1 as a function of time.

The spectra collected from the centre of the intermetallic show slight changes. Firstly the intensity of the C Kα peak increases after 8 hours and increases further after 16 hours. Quantification shows a significant increase in the carbon concentration after these times. This was the result of the deposition of carbon contamination from the test solution after 4 hours and because the EDX point spectra for these analyses were acquired from closer to the damaged region, which was rich in carbon material. The second most noticeable change is the presence of a weak Cu Lα peak after 8 hours, which remains after 16 hours. Quantification reveals there to be ~0.6 at.% copper. This copper is also observed in the AES point spectra, indicating it is at the surface of the intermetallic.

Figure 6.10 EDX spectra collected from the centre of Intermetallic #1 as a function of time.
The final spectra collected after 32 hours were acquired from the centre of the dome feature in the SEM micrograph so as to overlap with the position of the inclusion. None of the expected peaks for the intermetallic are observed in this spectrum, showing that the dome completely attenuates the signal from the intermetallic. Weak Al Kα, Si Kα and Cl Lα peaks were observed in this spectrum together with an intense O Kα. EDX point spectra were also collected from the dome after 64 hours during an examination of the surface in the JEOL SEM. These spectra were of much greater intensity than those shown here and so have not been included in the stacked spectra as they did not show additional compositional information about the dome.

Table 6.3 Quantification of the EDX spectra, normalised to 100%, collected from the centre of Intermetallic #1

<table>
<thead>
<tr>
<th>Time/composition (at.%)</th>
<th>Be</th>
<th>C</th>
<th>O</th>
<th>Al</th>
<th>Si</th>
<th>Fe</th>
<th>Cr</th>
<th>Mn</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>1.9</td>
<td>15.4</td>
<td>43.2</td>
<td>5.1</td>
<td>28.2</td>
<td>2.6</td>
<td>3.5</td>
<td>ND</td>
</tr>
<tr>
<td>15 min</td>
<td>-</td>
<td>1.6</td>
<td>15.1</td>
<td>43.8</td>
<td>5.1</td>
<td>26.2</td>
<td>3.4</td>
<td>4.8</td>
<td>ND</td>
</tr>
<tr>
<td>8 hours</td>
<td>-</td>
<td>15.0</td>
<td>9.7</td>
<td>36.5</td>
<td>4.8</td>
<td>24.9</td>
<td>3.6</td>
<td>4.6</td>
<td>0.6</td>
</tr>
<tr>
<td>16 hours</td>
<td>-</td>
<td>23.1</td>
<td>7.9</td>
<td>33.4</td>
<td>4.4</td>
<td>22.8</td>
<td>3.5</td>
<td>4.3</td>
<td>0.6</td>
</tr>
</tbody>
</table>

In addition to the EDX point spectra, EDX maps were collected from the intermetallic, they are arranged in columns of time 0, 15 min, 8 hours, 16 hours, 32 hours and 64 hours. These are shown in Figure 6.11. The magnification was reduced after 16 hours to ensure the entire region of interest could be mapped. The final map was collected using the JEOL SEM and so has a different aspect ratio. Additional scale bars are included in the images which refer to the column above. The manganese map has been omitted because of the Cr Kβ-Mn Kα peak overlap which results in the manganese map perfectly tracking the behaviour of the chromium map.

The maps of the elements present in the intermetallic, aluminium, iron, silicon and chromium show that the bulk of the intermetallic does not change in size up until the maps collected after 32 hours when the intermetallic is obscured by the dome. The carbon maps closely follow the oxygen map as a result of poor background removal at the low energy region of the spectrum. However, the carbon map does reveal that significant amounts of carbonaceous material are present in the damaged region of the intermetallic that remains until the region is observed by the dome. This material may have been contamination introduced during polishing.

The maps reveal that the corrosion products initially deposited around the intermetallic in the ring are rich in oxygen and contain some carbon. The products must therefore, contain beryllium as the counter ion to oxygen as no other elements are present. The maps also reveal that the dome primarily consists of oxygen with the incorporation of some carbon and chlorine. This suggests that the corrosion products are likely to be beryllium oxide or hydroxide back deposited from the test solution.

The beryllium maps show that the yield of Be Kα x-rays is from the corrosion products is poor because the rings of deposited material appear as regions of low counts in the maps. This shows that the corrosion products are voluminous as there is insufficient material to generate a strong x-ray signal, as is the case for the denser matrix. This is not observed in the oxygen maps because oxygen has a much higher x-ray yield.
compared to beryllium. These maps also show that no corrosion products are deposited onto the inclusion itself as an inner circle of the beryllium matrix is still observed.

Figure 6.11 EDX maps as a function of time collected from Intermetallic #1. (a) SEM micrograph, (b) Be, (c) O, (d) Al, (e) Si, (f) Fe, (g) Cr, (h) C and (i) Cl.
AES point spectra were acquired from the surface of the intermetallic, the matrix and the corrosion products. Survey spectra were collected in addition to high resolution beryllium spectra. Additionally, regions of specific spectral interest were also acquired. The survey spectra from the centre of the intermetallic are shown in Figure 6.12 (a). They show that the surface of the intermetallic is gradually covered with a layer of beryllium and oxygen containing material because the Al KLL and Fe LMM peaks from the intermetallic are completely attenuated and are no longer observed in the spectra collected after 8 hours and 16 hours. A moderately intense C KLL peak is observed in the spectrum collected after 4 hours. This shows that some hydrocarbon contamination remained after UV-Ozone cleaning. The peak is no longer observed in the spectrum from 8 hours. This also indicates that the surface has been covered by a layer of material. This effect is observed for all the subsequent inclusions and is believed to be a result of the rinsing stage prior to analyses causing beryllium hydroxide corrosion products to flow over the entire surface, a thin film of which adsorbs onto the entire surface.

The high resolution beryllium Auger transition (b) shows some slight changes to the structure of the Auger transition. For the first 4 hours there is little change in the appearance of the peak. However, there is a reduction in the intensity of the metal component between 4 hours and 8 hours of immersion and after 16 hours the metallic peak component is not present.

The high resolution Cu LMM spectra show the presence of copper at the surface of the intermetallic after 8 hours which remained on the surface after 16 hours. Longer acquisition did not lead to a significant improvement in the signal to noise and acquiring the peak with a higher retard ratio resulted in it not being

![Figure 6.12 AES spectra collected from the centre of Intermetallic #1 as a function of time. (a) Survey spectra, (b) high resolution beryllium Auger transitions and (c) high resolution Cu LMM spectra.](image)
resolved from the background. Therefore, it proved difficult to obtain a high quality spectrum from which reliable chemical state information could be obtained. However, the spectrum with the best signal to noise showed the peak to be centred at $\sim 917$ eV consistent with copper (II) oxide.

AES point spectra were also acquired from the nearby matrix and the corrosion products after 8 hours. Survey spectra and high resolution beryllium spectra are shown in Figure 6.13. The survey spectra (a) from the matrix (0 - 4 hours) all appear to be similar, with the largest change the appearance of the C $KLL$ after 4 hours. The survey spectra from the corrosion products also only show beryllium and oxygen to be present. This is in contrast to the EDX spectra which appear to show that carbon is associated with the deposited material.

The high resolution beryllium spectra (b) show no notable change in the spectrum after 15 minutes. However after 4 hours there is a slight drop in the intensity of the metallic peak component. This is the result of the thin layer of hydrocarbon contamination on the surface which attenuates the metal Auger electrons slightly more than the oxide Auger electrons. The spectra collected from the corrosion products after 8 and 16 hours shows a broad oxide peak shape with no metallic peak component. The spectra exhibit slight charging and are shifted $\sim 3$ eV to lower kinetic energy.

![Figure 6.13 AES spectra from the matrix (0-4 hours) and corrosion products (8 hours-16 hours) as a function of time. (a) Survey spectra and (b) high resolution beryllium Auger transitions.](image)

AES point spectra were also acquired from the surface of the dome. These were plotted separately to the other spectra because the signal intensity was so much greater because of some sample charging. The spectra are shown in Figure 6.14. The survey spectrum (a) shows that the only elements that are present at the surface with a detectable concentration are beryllium and oxygen. This is in contrast the to the EDX spectra which showed carbon and chlorine to be associated with the corrosion products. The beryllium Auger transition (b) appears to show both metal and oxide peak components. Being at the surface of corrosion products precipitated from solution it is unlikely that metallic beryllium is actually present and so it is thought that the Auger transition for beryllium hydroxide contains a metal like peak component. Despite observing trace levels of chlorine in the corrosion products by EDX the Cl $LMM$ region (c) does not show any chlorine to be present at the surface.
SAM maps were acquired from Intermetallic #1 at time zero, 15 min, 8 hours and 16 hours. Unfortunately, as a result of a technical problem 8 hour map became corrupted and unrecoverable. The maps from time zero, 15 min and 16 hours are shown in Figure 6.15. The maps are in agreement with the point spectra collected from the intermetallic and the matrix which show that there is little change to the surface after 15 minutes of immersion. The Si LMM and the Be KV overlap in kinetic energy at ~93 eV. Despite the lower signal intensity, the Si KLL was also included in mapping to try and separate the beryllium rich region from the silicon rich region. The surface of the intermetallic is rich in iron, aluminium and silicon and is poor in beryllium and oxygen compared to the matrix. The carbon associated with the damaged region is clearly distinguished from the background.

The signal to noise of the maps collected after 16 hours are adversely affected by the topography of the corrosion products. The regions facing the detector result in an intense signal while the regions in shadow result in noise. Even through the use of a data processing algorithm, which helps mitigate topographic differences, the maps are plagued with high levels of noise. The beryllium map appears to show the entire surface, even the region of the intermetallic to be rich in beryllium. This fits with the point spectra collected from the intermetallic, which showed only beryllium and oxygen. The oxygen map shows that the corrosion products and the surface of the intermetallic are poor in oxygen compared to the matrix. However, while the intensity of oxygen on the intermetallic does appear to be low in the point spectra, the corrosion products consist of beryllium and oxygen and should have a relatively strong oxygen intensity. This weaker oxygen intensity may be a consequence of slight charging of the corrosion products during analysis. This is apparent...
in the point spectra which show a peak shift to lower kinetic energies. This would result in poor mapping of the peak positions during SAM.

The most interesting map is that of copper. This map reveals the extent of copper deposition on the surface of the intermetallic, highlighting that the point spectra are representative of the intermetallic surface.

Figure 6.15 SAM maps of Intermetallic #7 as a function of time. (a) SEM micrograph, (b) Fe LMM, (c) Al KLL, (d) Be KLL/Si LMM, (e) O KLL, (f) Si KLL, (g) C KLL and (h) Cu.
To better illustrate the structure of the dome feature the sample was tilted within the spectrometer and an SEM micrograph acquired of the dome. This is shown in Figure 6.16. The figure highlights how sudden the influence of the particle falls away. The amount of corrosion products that are deposited around the particle does not show a linear reduction. A few loose flakes of material are observed around the dome and randomly distributed on the metal surface but the edge of the dome appears to mark the edge of activity around the particle.

![Figure 6.16 SEM micrograph of Intermetallic #1 after 32 hours immersion.](image)

**6.4.3 Intermetallic #2**

**6.4.3.1 Initial analysis**

The second intermetallic chosen for further analysis is shown in Figure 6.17 (a). The intermetallic had a regular geometry compared to Intermetallic #1 and was of a similar size. EDX phase analysis was performed on the x-ray maps collected from the SEM FOV and the resulting phase maps are shown in Figure 6.17 (b-d). The analysis shows that the matrix (b) is littered with small oxide inclusions (c). It also shows that the main body of the intermetallic (d) is homogeneous and extends subsurface almost doubling that size that is observed in the SEM micrograph.

![Figure 6.17 Phase analysis of the EDX maps collected using the JEOL SEM from Intermetallic #2. (a) SEM micrograph, (b) beryllium metal matrix, (c) BeO inclusions and (d) main AlFeBe₄ intermetallic.](image)
An EDX point spectrum was acquired from the centre of the intermetallic and is shown in Figure 6.18. The spectrum shows that the particle contains aluminium, silicon, iron, chromium and a trace of manganese. Small C Kα and O Kα peaks are observed in the spectrum as a result of contamination and surface oxide respectively. A small aluminium sum peak is observed at 2.98 keV, an aluminium and iron sum peak is also observed at ~2.1 keV.

Figure 6.18 EDX spectrum from the centre of Intermetallic #2.

Following the acquisition of the EDX spectra quantification was performed and this is shown in Table 6.4. The table shows quantification performed with and without including carbon, beryllium and oxygen from the inclusion composition. Quantification shows that the composition of the particle is consistent with an AlFeBe₄ precipitate, having an excess of aluminium, additional silicon and traces of chromium and manganese.

Table 6.4 Quantification from Intermetallic #2, normalised to 100%. Values with and without carbon and oxygen are shown

<table>
<thead>
<tr>
<th>Composition</th>
<th>Be</th>
<th>C</th>
<th>O</th>
<th>Al</th>
<th>Si</th>
<th>Fe</th>
<th>Cr</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intermetallic (at.%)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>52.2</td>
<td>6.9</td>
<td>39.2</td>
<td>0.9</td>
<td>0.8</td>
</tr>
<tr>
<td>Intermetallic (at.%)</td>
<td>-</td>
<td>4.7</td>
<td>9.2</td>
<td>44.8</td>
<td>5.8</td>
<td>34.0</td>
<td>0.8</td>
<td>0.7</td>
</tr>
</tbody>
</table>

AES spectra were collected from the same point in the centre of the particle as the EDX spectra. The survey spectrum, in addition to high resolution Be KLL and Al KLL spectra are shown in Figure 6.19 (a-c). The survey spectrum (a) shows that the surface of the particle is relatively free from hydrocarbon contamination. The main peaks present are Be KLL, O KLL, Al KLL and Fe LMM. The high resolution spectra (a + b) show that the surface of the particle has a thin oxide layer of BeO with a small amount of Al₂O₃.
6.4.3.2 Analysis as a function of time

The intermetallic was monitored following each corrosion step using AES and EDX point spectra and SEM imaging. Figure 6.20 (a-j) shows the SEM micrographs collected from Intermetallic #2 after each corrosion step from time zero (a) to 128 hours (j). No significant change is observed on or around the intermetallic throughout the investigation. The random deposition of corrosion products on the surrounding surface is apparent after 16 hours (g), this material does not appear to be associated with the intermetallic. The small white particles observed on and around the particle in (i + j) were believed to be silver nanoparticles from conductive silver paint used to adhere the sample to a sample holder. These were found to be randomly distributed over the surface after 64 hours and are also observed in the SEM micrographs collected from Intermetallics #5 and #6.
AES spectra were collected from the centre of the particle throughout the investigation. The spectra collected after 0, 15 min, 4 hours, 16 hours and 32 hours are shown in Figure 6.21. The survey spectra (a) show the gradual reduction in the intensity of the Fe \textit{LMM} and Al \textit{KLL} Auger peaks as the immersion time increases. After 16 hours of immersion, the peaks are no longer observed, although the Al \textit{KLL} is still observed in the high resolution spectrum (c). Despite the change in the survey spectra little change is observed in the Be \textit{KLL} spectra which shows beryllium metal and oxide peak components following each immersion time with similar intensities. The spectra indicate that material containing beryllium and oxygen gradually accumulates on the sample surface that attenuates the Auger electrons from the intermetallic.
Figure 6.21 AES spectra collected from Intermetallic #2 after different immersion times in NaCl solution. (a) survey spectra, (b) high resolution beryllium Auger transitions, (c) high resolution Al KLL spectra.

EDX spectra were acquired from the same position as the AES spectra and following the same immersion times, these are shown in Figure 6.22. The spectra show no change in appearance throughout the investigation. The intensity of the Al Kα, Fe Kα, and Si Kα peaks remain fairly constant. A slight drop in the intensity of all the x-ray peaks is observed in the spectrum collected after 15 minutes this is a result of a lower live time for this spectrum. The absence of any change shows that no change occurs to the bulk of the intermetallic during the immersion time.

Figure 6.22 EDX spectra collected from Intermetallic #2 after different immersion times in NaCl solution.
6.4.4 Intermetallic #3

6.4.4.1 Initial analysis

The third intermetallic chosen for analysis is shown in Figure 6.23 (a). The intermetallic was selected as it appeared to be the largest AlFeBe₄ intermetallic within the indented grid. The shape of the intermetallic was also irregular, being fairly long and extended, like many other AlFeBe₄ precipitates. EDX phase maps were generated from the raw x-ray count maps and are shown in Figure 6.23. They show the beryllium metal matrix (b), oxide particles dispersed along grain boundaries (c), the main AlFeBe₄ precipitate (d) and a small titanium-silicon inclusion (e).

![Figure 6.23 Phase analysis of the EDX maps collected using the JEOL SEM from Intermetallic #3.](image)

An EDX point spectrum was collected from the centre of the intermetallic and is shown in Figure 6.24. The spectrum is almost identical to the spectrum acquired from Intermetallic #2. It shows that the particle contains aluminium, silicon and iron together with a small concentration of chromium and manganese. A small aluminium sum peak is observed at 2.98 keV and aluminium and iron sum peaks are also observed at ~2.1 keV and ~8 keV.

![Figure 6.24 EDX spectrum from the centre of Intermetallic #3 prior to the first corrosion step.](image)
Quantification of the EDX data was performed and is shown in Table 6.5. Like the spectrum, the results are almost identical to those obtained from Intermetallic #2. Quantification shows that the particle is an AlFeBe₄ precipitate with an excess of aluminium, additional silicon and traces of chromium and manganese.

Table 6.5 Quantification from Intermetallic #3, normalised to 100%. Values with and without carbon and oxygen are shown

<table>
<thead>
<tr>
<th>Composition</th>
<th>Be</th>
<th>C</th>
<th>O</th>
<th>Al</th>
<th>Si</th>
<th>Fe</th>
<th>Cr</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intermetallic (at.%)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>53.5</td>
<td>5.6</td>
<td>39.1</td>
<td>1.2</td>
<td>0.6</td>
</tr>
<tr>
<td>Intermetallic (wt.%)</td>
<td>-</td>
<td>2.1</td>
<td>7.3</td>
<td>48.4</td>
<td>5.0</td>
<td>35.6</td>
<td>1.1</td>
<td>0.5</td>
</tr>
</tbody>
</table>

The AES survey spectrum and high resolution Be KLL and Si KLL spectra collected from the centre of the intermetallic are shown in Figure 6.25 (a-c). The survey spectrum (a) shows that the only elements present at the surface were beryllium, carbon, oxygen, aluminium and iron. A trace of nitrogen is also apparent by a small peak at ~400 eV. The high resolution spectra (a + b) show that the surface of the particle has a thin layer of beryllium oxide. This is thinner than the oxide observed to be present on Intermetallic #1 because the beryllium metal Auger peak component is more intense. The high resolution Al KLL shows only a weak metallic peak and so aluminium does not appear to be present in the oxide layer.

To confirm the size of the intermetallic, a SAM map of the O KLL peak was collected. The resulting map and the SEM micrograph of the region are shown in Figure 6.26. The SAM map shows that the entire bright region observed in the SEM micrograph is not exposed at the surface. This is highlighted by the red arrow in (b). Here, the oxygen intensity is lower than the surrounding metal surface but not as low as on the exposed intermetallic, which is revealed by the particularly dark regions in the map.
6.4.4.2 Analysis as a function of time

The intermetallic was monitored following each corrosion step using point AES spectra, EDX point spectra and SEM imaging. Figure 6.27 (a-j) shows the SEM micrographs collected from Intermetallic #3 after each corrosion step from time zero (a) to 128 hours (j). Some slight changes are observed in the series of micrographs. A dark halo is observed between 4 hours and 8 hours of immersion. This halo is pyrolised carbon from contamination present on the surface after 4 hours. The small dark circles observed on the intermetallic are also carbon pyrolised by the beam. The material in these small circles was so thick that the UV-Ozone cleaning that the sample underwent after 4 hours was not sufficient to remove all of the carbon contamination. Between 8 hours and 16 hours significant amounts of loose material are observed all over the surrounding matrix. These gradually increase throughout the remainder of the investigation but do not appear to be related to the presence of the intermetallic.
The AES spectra collected from the intermetallic are shown in Figure 6.28. The survey spectra shown in (a) show an apparent increase in the intensity of the Fe LMM and Al KLL peaks after 15 minutes. This was thought to be a result of the point spectra position changing slightly. The spectrum after 4 hours shows an intense C KLL peak. This reveals the significant amount of carbon contamination that was deposited onto the surface after this immersion step. At this point, the sample was UV-Ozone cleaned, resulting in a significant decrease in the contamination thickness. The remaining survey spectra only show the Be KLL, the C KLL and the O KLL peaks. The high resolution beryllium Auger region (b) shows a reduction in the intensity of...
the metallic component after 15 minutes, this is accompanied by an increase in the intensity of the Al KLL shown in (c). Both of the Auger transitions are then completely attenuated by the contamination layer as no peaks are observed. The spectra collected following longer immersion are similar to the spectra collected from Intermetallic #2, with the gradual removal of all peaks apart from the Be KLL and the O KLL.

![Figure 6.28 AES spectra collected from Intermetallic #3 after different immersion times in NaCl solution. (a) Survey spectra, (b) high resolution beryllium Auger transitions, (c) high resolution Al KLL spectra.](image)

EDX spectra acquired from the intermetallic are shown in Figure 6.29. The spectra show no change in the appearance of the spectrum until after 4 hours of immersion. At which point an intense in the intensity of the C Kα is observed. Additionally, an increase in the intensity of the O Kα is also observed. This was caused by the carbon contamination deposited during the immersion. The carbon intensity decreases throughout the remainder of the experiment. Apart from the carbon, no other changes are observed to the spectrum throughout the remainder of the investigation.
6.4.5 Intermetallic #4

6.4.5.1 Initial analysis

Although the particle studied in this section appears to be a mixed phase inclusion it has been named Intermetallic #4 for consistency with the other second phase particles that were studied. To acquire suitable AES spectra from the centre of the inclusion a higher primary beam energy than was used for the other intermetallic was required. By switching from a 10 keV to a 15 keV beam energy it was possible to obtain spectra from the particle almost free of charging. This occurs as the interaction volume from the 15 keV beam is generated further into the material and so a large number of secondary electrons that would have been generated within the insulating inclusion, with a lower energy beam, are generated within the matrix below it. These electrons are then grounded resulting in a low level of charging. The phase maps were generated from the EDX maps but these were found to slightly mask some of the internal structure of the intermetallic and so the phase map has been replaced with the net counts EDX maps. These are shown in Figure 6.30. The SEM micrograph of the FOV is shown in (a). The beryllium map (b) appears to show that little or no beryllium is present in the inclusion. Based upon the appearance of the maps (c-g) the particle is not homogeneous, containing a mix of carbon, oxygen, aluminium and silicon. AlFeBe₄ precipitates are also observed within the FOV.
An enlarged SEM micrograph is shown in Figure 6.31. This shows that the internal structure of the intermetallic is heterogeneous with a number of cracks throughout. The particle also has a well-defined edge. The sharpness of this edge indicates that it was produced through fracture and that some of the particle was removed during the polishing process. The oxygen and carbon rich material appears to be the darker grey platelets in the right side and bottom left of the particle while the aluminium rich area is the middle region.

In addition to the initial EDX map, EDX point spectra were also acquired from the centre of the intermetallic and the AlFeBe precipitates nearby. The spectra are shown in Figure 6.32. Quantification was performed...
from the spectra and is shown in Table 6.6. The spectrum shows intense O Kα and Al Kα x-ray peaks together with weaker C Kα and Fe Lα peaks. The spectrum and the composition of the precipitate are consistent with those observed for Intermetallics #1, #2 and #3. The composition of the intermetallic is particularly unusual as it appears to contain a large concentration of oxygen without a suitable corresponding counter ion to account for the 75 at.% oxygen.

Therefore, based upon this observation and the elemental distribution in the EDX maps, it appears that the intermetallic might be a mixed phase beryllium carbide/alumina particle. The carbon, and more so the beryllium x-rays are absorbed within the sample resulting in a poor spectral representation of the true carbon and beryllium content in the particle. Exposure to the atmosphere following polishing would hydrolyse the carbide turning it to beryllium oxide/hydroxide, which could explain the high oxygen content.

Table 6.6 Quantification from Intermetallic #4 and the nearby AlFeBe₄ intermetallics normalised to 100%. Values with and without carbon and oxygen are shown

<table>
<thead>
<tr>
<th>Composition</th>
<th>Be</th>
<th>C</th>
<th>O</th>
<th>Al</th>
<th>Si</th>
<th>Fe</th>
<th>Cr</th>
<th>Mn</th>
<th>Ni</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intermetallic Al₂O₃</td>
<td>-</td>
<td>-</td>
<td>75.5</td>
<td>20.5</td>
<td>3.7</td>
<td>0.1</td>
<td>ND</td>
<td>ND</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Intermetallic AlFe</td>
<td>-</td>
<td>-</td>
<td>53.2</td>
<td>6.5</td>
<td>6.5</td>
<td>0.1</td>
<td>ND</td>
<td>ND</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Intermetallic Al₂O₃</td>
<td>-</td>
<td>3.7</td>
<td>73.6</td>
<td>19.1</td>
<td>3.4</td>
<td>0.1</td>
<td>ND</td>
<td>ND</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Intermetallic AlFe</td>
<td>-</td>
<td>3.8</td>
<td>6.4</td>
<td>47.7</td>
<td>5.8</td>
<td>33.4</td>
<td>1.1</td>
<td>1.8</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

The AES spectra collected from the two positions highlighted in Figure 6.31 are shown in Figure 6.33. Each of the spectra collected from the edge were affected by slight sample charging and so the spectra in the figure are ~6 eV too low in kinetic energy, although they still provide chemical state information. The survey spectra (a) show that in both regions beryllium, oxygen, aluminium and silicon are the only elements present at the surface. The high resolution Si KLL spectrum (b) shows that elemental and oxide forms of silicon are present at the centre and edge of the inclusion. The beryllium spectrum (c) shows beryllium oxide to be present at both regions with no metallic components in the spectra. The high resolution Al KLL spectra show that metallic aluminium and aluminium oxide are present at the centre of the inclusion but only aluminium oxide is present at the edge.
**6.4.5.2 Analysis as a function of time**

The SEM micrographs collected from Intermetallic #4, after each immersion step, are shown in Figure 6.34 (a-j). They show the appearance of the intermetallic from time zero (a) to 128 hours (j). Little change is observed until 4 hours. The small dark patches on the matrix are carbon contamination. The change in the brightness from the centre of the intermetallic between 45 min (c) and 2 hours (d) was the result of switching off the secondary electron detector bias for imaging. Between 4 hours (e) and 8 hours (f) of immersion a change on the matrix around the inclusion is observed. Again as observed for Intermetallic #1, clusters of material encircle the inclusion and appear to have a constant distance from the centre of the particle. Less material is observed at the thinner bottom of the particle than the wider top. Additionally, the surface of the matrix immediately adjacent to the particle appears to be brighter than the surrounding matrix. Between 8 hours (f) and 16 hours (g) a ring of deposited material is observed further away from the inclusion and no further material was observed to deposit on the matrix where it was previously. The amount of material in this ring increases after 32 hours (h) with no additional material in the centre or on the intermetallic itself. Between 32 hours and 64 hours (i), material begins to deposit at the interface between the intermetallic and the matrix but not on the centre of the intermetallic. This material builds up further between 64 hours and 128 hours (j) with additional material in the central ring.
EDX spectra were collected from the centre of the intermetallic and the local matrix or the corrosion products, once they had formed, following each immersion. The EDX spectra collected from the matrix are shown in Figure 6.35 and the spectra collected from the intermetallic are shown in Figure 6.36. Quantification was performed on the spectra collected from the intermetallic and the results are shown in Table 6.7. Quantification was not performed on the spectra collected from the matrix and the corrosion products. The spectra collected from the matrix and the corrosion products are consistent with bulk beryllium and those collected for Intermetallic #1. Weak Be Kα and O Kα peaks are observed on a large background.
After 8 hours the spectra were collected from the corrosion products. These showed an intense O Kα peak as well as a weaker C Kα peak. As the immersion time increases the intensity of the Cl Kα also increases.

![Figure 6.35 EDX spectra collected from the matrix (0 and 15 min) and the corrosion products surrounding Intermetallic #4 as a function of time.](image)

The spectra collected from the centre of the intermetallic show only slight changes in appearance. Without the quantification it is difficult to determine if any changes have occurred with longer immersion. The same increase in the intensity of the C Kα that was observed for Intermetallic #1 is also observed in the EDX spectra after 8 hours. The most significant change is between the initial spectrum and the spectrum collected after 15 minutes. This shows a large decrease in the oxygen concentrations with a corresponding increase in the aluminium intensity. This reduction shifts the concentrations to be more consistent with an alumina/silica particle. This change could be caused by the loss of beryllium and oxygen containing species or by a slight shift in the position from which the EDX spectra were acquired. As can be seen by the initial EDX maps the area rich in oxygen is close to the centre of the intermetallic. However, the aluminium rich area is also close to this. A slight shift upwards in the analysed spot would result in the aluminium rich area being analysed.

![Figure 6.36 EDX spectra collected from the central region of Intermetallic #4 as a function of time.](image)

Following this significant change in the quantification, the remaining spectra and resulting quantification all appear to agree well, suggesting no changes to the intermetallic. Unlike Intermetallic #1 no copper was
observed in the EDX spectra collected from Intermetallic #4. However, a trace of chlorine was detected from the centre of the intermetallic.

Table 6.7 Quantification of the EDX spectra, normalised to 100%, collected from the centre of Intermetallic #4

<table>
<thead>
<tr>
<th>Time/Composition (at.%)</th>
<th>Be</th>
<th>C</th>
<th>O</th>
<th>Al</th>
<th>Si</th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>Cu</th>
<th>Ca</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>3.7</td>
<td>73.6</td>
<td>19.1</td>
<td>3.4</td>
<td>0.1</td>
<td>ND</td>
<td>0.1</td>
<td>ND</td>
<td>0.1</td>
<td>ND</td>
</tr>
<tr>
<td>15 min</td>
<td>-</td>
<td>2.2</td>
<td>55.8</td>
<td>34.5</td>
<td>6.1</td>
<td>1.2</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.2</td>
<td>ND</td>
</tr>
<tr>
<td>8 hours</td>
<td>-</td>
<td>11.3</td>
<td>48.9</td>
<td>32.2</td>
<td>6.1</td>
<td>1.4</td>
<td>ND</td>
<td>0.1</td>
<td>ND</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>16 hours</td>
<td>-</td>
<td>6.6</td>
<td>54.1</td>
<td>33.3</td>
<td>5.2</td>
<td>0.7</td>
<td>ND</td>
<td>0.1</td>
<td>ND</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>32 hours</td>
<td>-</td>
<td>7.2</td>
<td>53.7</td>
<td>34.1</td>
<td>3.6</td>
<td>1.1</td>
<td>ND</td>
<td>0.1</td>
<td>ND</td>
<td>0.1</td>
<td>0.2</td>
</tr>
</tbody>
</table>

EDX maps were also collected from the intermetallic. They are arranged in columns with time 0, 15 min, 8 hours, 16 hours, 32 hours and 64 hours. These are shown in Figure 6.37. The magnification was changed after 16 hours to ensure the entire region of interest could be mapped. The final map was collected using the JEOL SEM and so has a different aspect ratio and was also collected at a different magnification. Additional scale bars are included in the images which refer to the column above. The maps show the progressive changes in composition of the particle and the surrounding matrix as a function of time.

The beryllium maps show a similar pattern as the beryllium maps collected from Intermetallic #1. A dark ring forms after 8 hours which grows in width as the immersion time increases. This ring represents the corrosion products that are deposited onto the surface which attenuate the beryllium x-rays from the matrix. The inner region of the ring which remains bright in the maps showing the clear presence of beryllium matches well with the SEM micrographs which show a region free of corrosion products.

The maps of the elements present in the intermetallic appear to show little change up to 32 hours of immersion. The regions rich in aluminium, silicon, oxygen and carbon in the initial map remain so until 32 hours of immersion. After 64 hours of immersion, the amount of material in the ring of corrosion products has not increased but material rich in oxygen and possibly carbon have deposited at the matrix/particle interface. The absence of more material in the ring and appearance of material at the particle interface suggests the corrosion process changed between 32 hours and 64 hours of immersion.

The carbon signal appears to significantly reduce after 32 hours. If the carbon is associated with subsurface beryllium carbide it could mean that this had undergone hydrolysis to form beryllium oxide and methane, resulting in the removal of carbon. This would correspond to an increase in the oxygen intensity from these points, which does not occur. The likely explanation for the apparent reduction the intensity is the change in magnification. By increasing the FOV for the map the analysis time per point is reduced which has the effect of blurring the signal intensity. The carbon does appear to be associated with subsurface material as the maps collected using the JEOL SEM after 64 hours show little carbon from the intermetallic. This is caused by the beam striking the corrosion products first and scattering, reducing the depth of analysis at the intermetallic surface.
A weak chlorine signal is observed to be associated with the intermetallic after 8 hours which is consistent with the EDX point spectra. The intensity of the signal appears to remain fairly constant until 32 hours of immersion, at which point the chlorine signal is heavily isolated to the material at the rim of the intermetallic.

Figure 6.37 EDX maps as a function of time collected from Intermetallic #4. (a) SEM micrograph, (b) Be, (c) O, (d) Al, (e) Si, (f) Fe, (g) C and (h) Cl.
The Auger spectra collected from Intermetallic #4 are shown in Figure 6.38. The survey spectra are shown in (a) and reveal that aluminium and silicon are present at the surface of the intermetallic initially and remain so until 4 hours of immersion. The intensity of the Al KLL and Si KLL falls significantly after 8 hours but they are still noticeable above the noise until after 16 hours of immersion. After 32 hours, the aluminium and silicon Auger transitions are no longer observed but the Cu LMM peaks are clearly present above the background.

The initial high resolution beryllium Auger transition (b) and the spectrum collected after 15 minutes are both affected by severe sample charging and have a weak intensity despite performing a normalisation on the spectra in this figure. However, they both show only oxide peak components. The charging is also observed in the survey spectra, with a noticeable shift to a higher kinetic energy, compared to the spectra collected after longer immersion times. After 4 hours the spectra remain fairly constant showing the characteristic peak shape for beryllium oxide.

The high resolution Cu LMM spectra (c) show the presence of copper at the surface of the intermetallic after 8 hours which remained on the surface after 32 hours. As for Intermetallic #1, the peak position was centred at ~917 eV, which is consistent with copper (II) oxide.

![Figure 6.38 AES spectra collected from the centre of Intermetallic #4 as a function of time. (a) Survey spectra, (b) high resolution beryllium Auger transition and (c) high resolution Cu LMM.](image)

The Auger spectra acquired from the matrix and the corrosion products are shown in Figure 6.39. They are consistent with those acquired for Intermetallic #1. The survey spectra (a) and the beryllium Auger transition (b) from the matrix show no significant change up to 4 hours of immersion. The survey shows intense Be
$KLL$ and $O\ KLL$ transitions with a near constant intensity and the high resolution spectra show a fairly even peak intensity ratio between the oxide and metal peak components. The survey spectra from the corrosion products, after 8 hours and 16 hours, show only beryllium and oxygen to be present. The high resolution beryllium spectra show a broad oxide-like shape. The peak positions in the spectrum collected after 16 hours shows signs of charging as they are shifted to a lower kinetic energy. The spectrum appears to show metallic and oxide peak components. The slight charging is also apparent in the survey spectrum.

The survey spectrum collected after 32 hours was acquired from the surface of the voluminous corrosion products at the interface between the particle and the matrix. The spectrum shows beryllium and oxygen to be present. The Be $KLL$ region shows metallic and oxide peak components which is in agreement with the spectrum acquired from the dome covering Intermetallic #1.

The charging associated with Intermetallic #4 led to significant problems during SAM mapping. Charging resulted in random shifts of the primary peaks in the spectrum, as shown by the spectra in Figure 6.33. Because of this charging they could not be mapped effectively and the maps that were generated had high levels of noise, revealing little about the surface composition. One of the maps of particularly interest and of sufficient quality is shown in Figure 6.40 (b) together with the SEM micrograph (a). The map is of the Cu $LMM$ Auger transition after 16 hours. The map reveals the presence of a low concentration of copper on the intermetallic, as was also observed for Intermetallic #1.
As was performed for Intermetallic #1 an SEM micrograph was collected from the intermetallic to help illustrate the structure of the corrosion products. This is shown in Figure 6.41. Again the region of activity around the particle has a definite edge as the micrograph shows that the inner region of the ring is free of corrosion products while they build up at the edge of the ring.

6.4.6 Intermetallic #5

6.4.6.1 Initial analysis

After examining a number of the larger particles that appeared to be elemental silicon from the automated analysis, many were found to consist of precipitated AlFeBe₄ and silicon. They all appeared to have well defined interfaces with one another suggesting little intermixing of the phases. The fifth intermetallic that was selected represented the largest of these mixed phase inclusions that was located within the grid. EDX phase analysis was performed on the x-ray maps collected from the SEM FOV. The resulting phase maps are shown in Figure 6.42. The SEM micrograph is shown in (a), the dark circles are the result of carbon pyrolised onto the surface during EDX point analysis. The analysis shows that the matrix (b) is homogeneous and that small oxide inclusions are distributed along the grain boundaries (e). The phase analysis highlights the well-defined interface between the two phases of the particle. The sharp line in the middle phase maps
represents the interface between the two phases, this is observed in the AlFeBe₄, brighter side (c) and the
darker silicon side (d).

![Image](image1.png)

Figure 6.42 Phase analysis of the EDX maps collected using the JEOL SEM from Intermetallic #5. (a) SEM micrograph, (b) beryllium metal matrix, (c) AlFeBe₄ part of intermetallic, (d) silicon part of the intermetallic and (e) BeO inclusions.

EDX point analysis was performed on each side of the inclusion. The spectra from each side are shown in Figure 6.43 and the resulting quantification is shown in Table 6.8. The spectrum collected from the AlFeBe₄ precipitate shows a moderate concentration of silicon which is consistent with the amounts found to be present in Intermetallics #1, #2 and #3. However, it is possible that some of the silicon is present as a result of some overlap of the analysis volume with the silicon side of the inclusion. The aluminium to iron ratio appears to show a slight excess of iron in the precipitate, with more than any of the previously examined intermetallics. The spectrum from the silicon inclusion appeared to show a small concentration of aluminium and iron just as with the silicon in the AlFe side this could be caused by some overlap of the analysis volume with the AlFe side.

![Image](image2.png)

Figure 6.43 EDX spectra from the centres of each region of Intermetallic #5.
Table 6.8 Quantification from Intermetallic #5, normalised to 100%. Values with and without carbon and oxygen are shown

<table>
<thead>
<tr>
<th>Composition</th>
<th>Be</th>
<th>C</th>
<th>O</th>
<th>Al</th>
<th>Si</th>
<th>Fe</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intermetallic Si</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.6</td>
<td>96.6</td>
<td>1.8</td>
<td>ND</td>
</tr>
<tr>
<td>(at.%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intermetallic AlFe</td>
<td>-</td>
<td>2.2</td>
<td>2.6</td>
<td>43.2</td>
<td>5.8</td>
<td>50.0</td>
<td>0.9</td>
</tr>
<tr>
<td>(at.%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intermetallic Si</td>
<td>-</td>
<td>1.1</td>
<td>5.5</td>
<td>39.9</td>
<td>5.4</td>
<td>47.3</td>
<td>0.8</td>
</tr>
<tr>
<td>(at.%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

AES spectra were collected from the centre of each side of the particle. The survey spectra in addition to the high resolution Be $K\!\!L$ and the Si $K\!\!L$ spectra from both sides as well as the Al $K\!\!L$ spectrum from the AlFe side are shown in Figure 6.44 (a-c). The survey spectrum from the silicon side (a) shows a trace of nitrogen is present as well as the Be $K\!\!L$, O $K\!\!L$ and Si $K\!\!L$ Auger transitions. The high resolution spectra from this side (c + d) show that the surface of the particle has a thin oxide layer of SiO$_2$. The survey spectrum from the AlFe side (a) shows Be $K\!\!L$, O $K\!\!L$, Fe $LMM$, Al $K\!\!L$ and Si $K\!\!L$ Auger transitions. The high resolution spectra from this side (b + c) show the oxide is predominately beryllium oxide with a small amount of aluminium oxide.

Figure 6.44 AES spectra collected from Intermetallic #5 prior to exposure to the test solution. (a) Survey spectra, (b) high resolution Al $K\!\!L$ spectrum, (c) high resolution beryllium Auger transitions and (d) high resolution Si $K\!\!L$ spectra.

6.4.6.2 Analysis as a function of time

The intermetallic was monitored following each corrosion step using point AES spectra, EDX point spectra and SEM imaging. Figure 6.45 (a-j) shows the SEM micrographs collected from Intermetallic #5 after each experiment step from time zero (a) to 128 hours (j). The small black spots observed in the micrographs after 4 hours are pyrolised carbon from AES analysis. Corrosion products are observed to accumulate across the sample surface after 8 hours of immersion. Small white particles are observed around and on the
intermetallic after 64 hours. These are thought to be the silver particles previously discussed and observed on Intermetallic #2. They appeared to be randomly distributed across the sample surface.

![SEM micrographs of Intermetallic #5 as a function of immersion time in NaCl.](image)

Figure 6.45 SEM micrographs of Intermetallic #5 as a function of immersion time in NaCl. (a) Initial, (b) 15 min, (c) 45 min, (d) 2 hours, (e) 4 hours, (f) 8 hours, (g) 16 hours, (h) 32 hours, (i) 64 hours and (j) 128 hours.

AES spectra were collected from the centre of the silicon side throughout the investigation, a number of analysis times are shown in Figure 6.46. The survey spectra (a) show the gradual reduction in the intensity of the silicon Auger peaks as the immersion time increases. This is apparent by the gradual reduction in the Si $KLL$ peak intensity to the point where after 16 hours of immersion no clear Si $KLL$ peak is observed. The surface sensitive Be $KLL$ (b) shows a shift from silicon Auger peaks to beryllium Auger peaks between 4
hours and 16 hours of immersion. The less surface sensitive Si $\text{KLL}$ (c), shows the absence of the silicon peak, indicating the deposition of beryllium containing material on the intermetallic surface.

Figure 6.46 AES spectra collected from Intermetallic #5 after different immersion times in NaCl solution. (a) Survey spectra, (b) high resolution beryllium Auger transitions, (c) high resolution Si $\text{KLL}$ spectra.

The EDX spectra from the silicon side were acquired from the same position as the AES spectra and are shown in Figure 6.47. The spectra show intense Si $\text{K}\alpha$ peaks, weaker O $\text{K}\alpha$ and Al $\text{K}\alpha$ peaks and a silicon sum peak. No other x-ray lines are observed in the spectra and no change to the spectra are observed throughout the time sequence of exposure.

Figure 6.47 EDX spectra collected from the silicon side of Intermetallic #5 after different immersion times in NaCl solution.
The AES spectra collected from the AlFe side are shown in Figure 6.48. The survey spectra (a) show the same trend as observed for the silicon side with the gradual reduction in the intensity of the iron and aluminium Auger peaks as the immersion time increases. Between 4 hours and 16 hours of immersion these peaks are no longer observed in the survey, only the Be KLL and O KLL peaks remain. The surface sensitive high resolution beryllium Auger (b) shows a shift from predominately oxide to oxide and metal peak components throughout the investigation. The less surface sensitive Al KLL (c), shows a slight trace of aluminium remaining at the surface after 4 hours and further to 16 hours of immersion.

![AES spectra collected from Intermetallic #5 after different immersion times in NaCl solution. (a) Survey spectra, (b) high resolution beryllium Auger transitions, (c) high resolution Al KLL spectra.](image)

EDX spectra were also acquired from the AlFe side of the intermetallic and are shown in Figure 6.47. The spectra show intense Al Kα and Fe Lα peaks as well as weaker Si Kα and O Kα peaks. No significant changes are observed in the spectra throughout the investigation, apart from a slight increase in the intensity of the C Kα.
6.4.7 Intermetallic #6

6.4.7.1 Initial analysis

Although the particle studied in this section is a non-metallic inclusion it has been named Intermetallic #6 for consistency with the other second phase particles that were studied. Intermetallic #6 was an elemental silicon inclusion and is shown in Figure 6.50 (a). The solidification of the silicon may have nucleated from the oxide particle observed at the tip of the inclusion at the grain boundary. The silicon will have precipitated from the hot pressed beryllium. Phase maps of the intermetallic were generated from the EDX maps collected from the intermetallic prior to the onset of the corrosion investigation. The maps are shown in Figure 6.50. The maps reveal the presence of three distinct phases within the SEM FOV. These include: (b) the beryllium matrix, (c) beryllium oxide inclusions and (d) the silicon inclusion. The maps show the inclusion to be homogeneous in composition with oxide inclusions dispersed along nearby grain boundaries.

In addition to the EDX phase maps, EDX point spectra were acquired from the centre of the intermetallic. These are shown in Figure 6.51. The spectra show that the particle contains silicon with a trace of iron. Small C Kα and O Kα peaks are observed in the spectrum as a result of contamination and the surface oxide
respectively. The intensity of the Si Kα is such that a silicon sum peak is also present in the spectrum at ~3.5 keV.

![Figure 6.51 EDX spectrum from the centre of Intermetallic #6.](image)

Following the acquisition of the EDX spectrum quantification was performed and this is shown in Table 6.7. The table shows quantification performed with and without including carbon, beryllium and oxygen from the inclusion composition. Quantification shows that the inclusion is high purity silicon.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Be</th>
<th>C</th>
<th>O</th>
<th>Si</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intermetallic (at.%)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>99.9</td>
<td>0.1</td>
</tr>
<tr>
<td>Intermetallic (at.%)</td>
<td>-</td>
<td>4.7</td>
<td>12.1</td>
<td>82.1</td>
<td>0.3</td>
</tr>
</tbody>
</table>

AES spectra were collected from the same point in the centre of the particle as the EDX spectra. The survey spectrum in addition to high resolution Be KLL and Si KLL spectra are shown in Figure 6.52 (a-c). The survey spectrum (a) shows that a low level of contamination is present on the surface of the particle following UV-Ozone cleaning. A trace of nitrogen is apparent by a small peak at ~400 eV. The high resolution spectra (a + b) show that the surface of the particle has a thin oxide layer of SiO₂. This is apparent because of the small oxide components in the spectra.
Figure 6.52 AES spectra collected from Intermetallic #6 prior to exposure to the test solution. (a) Survey spectrum, (b) high resolution beryllium Auger transition, (c) high resolution Si KLL spectrum.

6.4.7.2 Analysis as a function of time

The sixth intermetallic was monitored in the same as way previous intermetallics, following each corrosion step AES and EDX point spectra were acquired together with an SEM micrograph. Figure 6.53 (a-j) shows the SEM micrographs collected from Intermetallic #6 after each corrosion step from time zero (a) to 128 hours (j). They show little apparent change to the structure of the intermetallic or to the surrounding matrix. The deposition of general corrosion products on the surrounding surface is apparent after 8 hours (f), this material does not appear to be associated with the intermetallic as it progressively builds up with a random distribution. The small white particles observed on and around the particle in (i + j) were thought to the same particles as observed for Intermetallic #2.
Figure 6.53 SEM micrographs of Intermetallic #6 as a function of immersion time in NaCl. (a) Initial, (b) 15 min, (c) 45 min, (d) 2 hours, (e) 4 hours, (f) 8 hours, (g) 16 hours, (h) 32 hours, (i) 64 hours and (j) 128 hours.

In addition to the SEM micrographs, AES spectra were collected from the centre of the particle. These are shown in Figure 6.54. The survey spectrum (a) is included to show an overview of the surface composition and the high resolution Be KLL (b) and Si KLL (c) spectra are shown as these peaks reveal chemical state information. The spectra show the gradual reduction in the intensity of the silicon Auger peaks as the immersion time increases. This is observed in the survey by the gradual reduction in peak intensity to the point where after 32 hours of immersion no clear Si KLL peak is observed. However, the Auger transition still has a significant influence on the spectral background. The surface sensitive Be KLL region (b) shows a shift from silicon LMM Auger peaks to beryllium KLL Auger peaks between 4 hours and 16 hours of...
immersion. This is not observed in the less surface sensitive Si $KLL$ (c), which shows a reduction in intensity but not complete absence of the silicon peak.

Figure 6.54 AES spectra collected from Intermetallic #6 after different immersion times in NaCl solution. (a) Survey spectra, (b) high resolution beryllium Auger transitions, (c) high resolution Si $KLL$ spectra.

EDX spectra were acquired from the same position as the AES spectra. The spectra shown in Figure 6.55 were collected following the same immersion times as the AES spectra. The spectra show an intense Si $K\alpha$ peak together with a weaker O $K\alpha$ peak and a silicon sum peak. No other x-ray lines are observed in the spectra. The spectrum collected after 15 minutes is more intense than the others because of a slightly longer spectral live time.

Figure 6.55 EDX spectra collected from Intermetallic #6 after different immersion times in NaCl solution.
6.4.8 Intermetallic #7

6.4.8.1 Initial analysis

The seventh inclusion was a single phase Ti₃Si particle with an associated subsurface AlFeBe₄ precipitate. An SEM micrograph of the intermetallic is shown in Figure 6.56 (a). The figure also shows the phase maps produced from the initial EDX data collected using the JEOL SEM. The maps reveal the presence of four phases within the SEM FOV. These include: (b) the beryllium matrix, (c) a subsurface AlFeBe₄ precipitate (d) the Ti₃Si intermetallic and (e) beryllium oxide inclusions. The maps show the intermetallic is homogeneous in composition with oxide inclusions dispersed along grain boundaries. The maps also reveal that the Ti₃Si intermetallics are likely to be present in the metal prior to the formation of the AlFeBe₄ precipitate because of the appearance of this phase at the sharp apex of the intermetallic in the map. The apex would provide a good nucleation point for a precipitating phase in the aged beryllium. It is possible to determine that this is subsurface because it is not observed in the SEM micrograph.

![Figure 6.56 Phase analysis of the EDX maps of Intermetallic #7. (a) SEM micrograph, (b) beryllium metal matrix, (c) subsurface AlFeBe₄ intermetallic (d) main Ti₃Si intermetallic and (e) BeO inclusions.](image)

An EDX point spectrum was acquired from the centre of the intermetallic and is shown in Figure 6.57. The spectrum shows intense Si Kα and Ti Kα peaks as well as weaker Zr Lα and Cr Kα peaks. Quantification of the spectrum is shown in Table 6.9. Carbon and oxygen have not been omitted from the table, as was performed for the other intermetallics as no carbon peak could be resolved from the noise. The O Kα overlaps strongly with the Ti Lα resulting in poor quantification of oxygen.
Figure 6.57 EDX spectrum from the centre of Intermetallic #7.

Table 6.9 Quantification from Intermetallic #7, normalised to 100%, ND represents an element that was not detected

<table>
<thead>
<tr>
<th>Composition</th>
<th>Be</th>
<th>C</th>
<th>O</th>
<th>Al</th>
<th>Si</th>
<th>Ti</th>
<th>Zr</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intermetallic (at.%)</td>
<td>-</td>
<td>ND</td>
<td>ND</td>
<td>0.5</td>
<td>21.5</td>
<td>71.5</td>
<td>2.1</td>
<td>4.3</td>
</tr>
</tbody>
</table>

AES spectra were also recorded from the centre of the intermetallic and are shown in Figure 6.58. The survey spectrum (a) shows that only beryllium, titanium, oxygen and a trace of silicon are present at the surface of the particle.

Small changes in the low kinetic energy side of the titanium peak (b) can be used to reveal chemical state information [108]. A differential form of the spectrum (not shown) indicates that titanium is in metallic form. The high resolution beryllium spectrum (c) shows that the oxide layer on the intermetallic is predominately beryllium oxide. This is because an intense oxide component and a weaker metallic component are observed in the spectrum. The spectra also show that metallic beryllium appears to be present in the intermetallic despite the EDX results. This agrees with the WDX results from Chapter 5 which showed beryllium to be associated with the Ti₃Si type intermetallics. Silicon (d) is also present but does not seem to be part of the oxide layer as it is not present as SiO₂.
6.4.8.2 Analysis as a function of time

The SEM micrographs collected from the seventh intermetallic, after each immersion step, are shown in Figure 6.59 (a-j). They show the appearance of the intermetallic from time zero (a) to 128 hours (j). Little change is observed until 4 hours and then between 4 hours (e) and 8 hours (f) of immersion a significant change is observed. As observed for the two previous active intermetallics, clusters of white material encircle the inclusion with fixed distance from the centre of the particle. After 16 hours (g) more material is deposited around the inclusion but not directly on it. A large mesh like structure of material is also observed on the right hand side of the particle. After 32 hours the same effect that was observed for Intermetallic #1 was observed to occur. A dome of corrosion products had formed from the previous circle of material that fully enveloped the intermetallic. From this point the two intermetallic show the same relationship with slightly more material observed to deposit on and around the dome after 64 hours (i) and then between 64 hours and 128 hours (h) little further change seems to occur.
Figure 6.59 SEM micrographs of Intermetallic #7 as a function of immersion time in NaCl. (a) Initial, (b) 15 min, (c) 45 min, (d) 2 hours, (e) 4 hours, (f) 8 hours, (g) 16 hours, (h) 32 hours, (i) 64 hours and (j) 128 hours.

As for the other active intermetallics EDX spectra were collected from the centre of the intermetallic, the local matrix and the corrosion products. The EDX spectra collected from the matrix are shown in Figure 6.60 and the spectra collected from the intermetallic are shown in Figure 6.61. Quantification was performed on the spectra collected from the intermetallic and the results are shown in Table 6.10. Quantification was not performed on the spectra collected from the matrix. The spectra collected from the matrix are consistent with bulk beryllium. They show an intense O Kα peak as well as a weaker C Kα peak. As the immersion time increases the concentration of chlorine associated with the products increases as shown by the increasing intensity of the Cl Kα.
Figure 6.60 EDX spectra collected from the matrix (0 and 15 min) and the corrosion products surrounding Intermetallic #7 as a function of time.

The spectra collected from the centre of the intermetallic show only small changes throughout the immersion time until the formation of the dome structure. Between the initial spectrum and the spectrum collected after 15 minutes there is no change in the spectrum of the quantification. Intense Si K and Ti Kα peaks are present together with weaker Zr Lα and Cr Kα peaks. The intensity of the C Kα increases in intensity in the spectrum collected after 8 hours of immersion, in agreement with the other active intermetallics. In addition to the increase in the carbon intensity a shoulder is observed on the Ti Lα peak which is the O Kα peak. This was present in the initial spectrum but was not resolvable from the Ti Lα peak and so quantification was unsuccessful. This oxygen is probably associated with a stray flake of corrosion product that can be observed on the surface of the intermetallic after 8 hours. The sudden increase in carbon and oxygen concentrations has the effect of changing the composition of the intermetallic reducing the silicon and tantalum concentrations. An additional change that occurs is the appearance of a small Cu Lα peak after 8 hours. The peak is close to the noise floor and cannot be clearly seen in the spectrum until after 16 hours, when the intensity and concentration have increased. The presence of copper at the intermetallic surface is consistent with the other active inclusions.

Figure 6.61 EDX spectra collected from the central region of Intermetallic #7 as a function of time.
The spectrum collected after 32 hours is from the centre of the dome. The spectrum shows an intense O Kα peak, a weaker C Kα peak together with a weak Cl La peak. The presence of a small Si Kα and Ti Kα peaks can also be observed by the slight change in the background intensity.

Table 6.10 Quantification of the EDX spectra collected from the centre of Intermetallic #7, normalised to 100%

<table>
<thead>
<tr>
<th>Time/Composition (at.%)</th>
<th>Be</th>
<th>C</th>
<th>O</th>
<th>Al</th>
<th>Si</th>
<th>Ti</th>
<th>Zr</th>
<th>Cr</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>ND</td>
<td>ND</td>
<td>0.5</td>
<td>21.5</td>
<td>71.5</td>
<td>2.1</td>
<td>4.3</td>
<td>ND</td>
</tr>
<tr>
<td>15 min</td>
<td>-</td>
<td>ND</td>
<td>ND</td>
<td>0.5</td>
<td>21.1</td>
<td>72.0</td>
<td>2.7</td>
<td>3.7</td>
<td>ND</td>
</tr>
<tr>
<td>8 hours</td>
<td>-</td>
<td>7.8</td>
<td>10.7</td>
<td>0.4</td>
<td>17.8</td>
<td>57.9</td>
<td>2.2</td>
<td>2.9</td>
<td>0.3</td>
</tr>
<tr>
<td>16 hours</td>
<td>-</td>
<td>2.2</td>
<td>12.1</td>
<td>0.5</td>
<td>17.6</td>
<td>60.2</td>
<td>1.5</td>
<td>5.0</td>
<td>0.9</td>
</tr>
</tbody>
</table>

EDX maps were collected from the intermetallic. They are arranged in columns of time 0, 15 min, 8 hours, 16 hours, 32 hours and 64 hours. These are shown in Figure 6.62. The magnification was changed after 16 hours to ensure the entire region of interest could be mapped. The final map was collected using the JEOL SEM and so has a different aspect ratio. This was also collected at a different magnification. Additional scale bars are included in the images which refer to the column above.

The maps show a similar behaviour as was observed in the EDX maps collected from Intermetallic #1. Firstly the beryllium maps show the same formation of a dark ring with a region of low intensity, formed as a result of corrosion products attenuating the matrix signal. This grows wider but leaves the inner region close to the intermetallic free of material, producing a region of intense signal. This region is then completely filled by the dome structure which shows no beryllium intensity.

The oxygen map shows the same ring as the beryllium maps but as a region of intense signal as the oxygen intensity is strong from the corrosion products. This ring forms at a constant distance away from the particle and remains until the formation of the dome, the circumference of which overlaps with the ring. As observed for Intermetallic #1 the dome appeared to be rich in oxygen and contained traces of carbon and chlorine.
Figure 6.62 EDX maps as a function of time collected from Intermetallic #7. (a) SEM micrograph, (b) Be, (c) O, (d) Al, (e) Si, (f) Ti, (g) Cr, (h) Fe, (i) C and (j) Cl.
The Auger point spectra collected from the centre of the intermetallic are shown in Figure 6.63. The survey spectra (a) are consistent with the spectra collected from Intermetallic #1 and show the gradual attenuation of the peaks from the elements in the intermetallic. In this case the Ti \textit{LMM}. The Si \textit{KLL} was close to the noise floor and is difficult to observe in the spectra. The attenuation length of the Si \textit{KLL} Auger electrons is much greater than that of the Ti \textit{LMM} electrons which shows that, because the silicon transition is not observed, the surface of the intermetallic is enriched in titanium and beryllium.

After 8 hours of immersion the Ti \textit{LMM} is no longer observed in the spectrum and only the Be \textit{KLL} and O \textit{KLL} remain together with a weak C \textit{KLL} peak. A slight deviation in the background is observed in the survey spectra collected after 8 hours and 16 hours at ~900 eV, the position at which the Cu \textit{LMM} is present. The spectrum collected after 32 hours was acquired from the centre of the dome structure. The only peaks that were observed to be present were the O \textit{KLL} and particularly weak Be \textit{KLL}.

The high resolution beryllium Auger transitions are shown in (b). No change is observed between the initial spectrum and the spectrum after 15 minutes. However, the spectrum collected after 4 hours appears to show a more intense metallic component. This could correspond to a thinning oxide layer on the inclusion. The metallic component then reduces in intensity to appear closer to the initial spectrum after 8 hours. The spectrum after 16 hours shows a significantly reduced signal intensity, indicating that the beryllium is no longer present at the extreme surface of the intermetallic. This is likely the result of some signal attenuation by the copper at the intermetallic surface. The spectrum collected after 32 hours was acquired from the dome...
structure and is consistent with the spectrum from the dome covering Intermetallic #1. It shows oxide and metal peak components, although the spectrum is affected by some sample charging shifting the peaks to a lower kinetic energy.

In agreement with the results from Intermetallic #1 and #4 copper is observed at the surface of the intermetallic after 8 hours (c). The intensity of the Cu $LMM$ increases after 16 hours, which is in agreement with the observations made from the SAM maps shown in the next section.

The Auger spectra acquired from the matrix and the corrosion products, once they had been deposited, are shown in Figure 6.64. They are consistent with those acquired for Intermetallic #1. The survey spectra (a) and the beryllium Auger transition (b) from the matrix show no change up to 4 hours of immersion. The survey shows intense Be $KLL$ and O $KLL$ transitions with a near constant intensity and the high resolution spectra show a fairly even peak intensity ratio between the oxide and metal peak components. A C $KLL$ peak is observed in the survey spectrum after 4 hours which was a consequence of the remaining carbon after UV-Ozone cleaning. The survey spectra from the corrosion products, after 8 hours and 16 hours, show only beryllium and oxygen to be present. The high resolution beryllium spectra show a broad oxide shape. The peak positions are also shifted to a lower kinetic energy. This explains the poor mapping quality of the Be $KLL$ and O $KLL$ transitions in the SAM maps shown in the next section. The peak broadening is a result of sample charging. The survey spectrum collected after 32 hours was acquired from the surface of the dome and show beryllium and oxygen to be present. The Be $KLL$ region shows metallic and oxide peak components which is in agreement with the spectrum acquired from the dome covering Intermetallic #1.

![Figure 6.64 AES spectra from the matrix (0-4 hours) and corrosion products (8 hours-32 hours) as a function of time. (a) Survey spectra and (b) high resolution beryllium Auger transitions.](image)

AES maps were acquired from the intermetallic prior to immersion, after 15 minutes, 8 hours and after 16 hours. These are shown in Figure 6.65. The same effect of the significant surface topography that affected the maps for this intermetallic affected the maps for Intermetallic #1. The majority of the maps show mostly noise after the onset of material deposition. No AES maps were acquired from the particle between 15 minutes and 8 hours of immersion as no visual or significant change in the AES spectra occurred from the matrix or the intermetallic. The initial maps show the surface of the particle rich in titanium and silicon and poor in oxygen and beryllium compared to the surrounding matrix. Small spots of high intensity are observed.
in the titanium map with corresponding low intensity spots in the beryllium and oxygen maps. These spots are thought to be caused by pyrolised carbon depositing at the positions where AES point spectra were acquired. No discernable change occurs between the maps collected from the initial surface and those collected after 15 minutes.

After 8 hours the titanium signal and the silicon signal from the intermetallic is completely obscured. The matrix and the intermetallic show no difference in the concentration of these elements. This agrees with the point spectra which show that the Ti \( LMM \) transition is completely attenuated by oxygen and beryllium containing material after 8 hours.

The beryllium and beryllium maps show a similar behaviour to one another. They both show an inner circle of apparently unaffected beryllium around the intermetallic. This region appears bright compared to the intermetallic and the surrounding halo associated with the deposition of corrosion products. The high signal intensity from this inner region suggests that the matrix is not attacked and no significant material deposited has occurred in the region. The intensity of this region is reduced as more corrosion products deposit around the inclusion after 16 hours. This material deposits much closer to the intermetallic than the material surrounding Intermetallic #1.

The same behaviour for copper is observed in the maps collected from the intermetallic as observed for Intermetallics #1 and #4. In agreement with the point spectra, copper is observed in the maps collected from the surface after 8 hours and after to 16 hours. The region of copper deposition appears to have grown between these two maps covering the intermetallic and a small region around it.
Figure 6.65 SAM maps of Intermetallic #7, as a function of time. (a) SEM micrograph, (b) Ti LMM, (c) Si KLL, (d) Be KLL/Si LMM, (e) O KLL and (f) Cu LMM.

An SEM micrograph was collected from the dome with the sample tilted and is shown in Figure 6.66. The brightness and contrast is poor and could not be corrected for as a result of the extremely high yield of secondary electrons from the voluminous corrosion products facing the SEM detector. This suppressed the intensity from the rest of the dome. The behaviour of the corrosion products around the intermetallic is similar to Intermetallic #1, with the amount of corrosion products around the particle not showing a linear
reduction. A few loose flakes of material are observed around the dome and are randomly distributed on the metal surface but the edge of the dome appears to mark the edge of activity around the particle.

Figure 6.66 SEM micrograph of the dome covering Intermetallic #7 after 32 hours of immersion.

6.4.9 Intermetallic #8

6.4.9.1 Initial analysis

Although the particle studied in this section is a ceramic inclusion it has been named Intermetallic #8 for consistency with the other second phase particles that were studied. Intermetallic #8, as shown in Figure 6.67 (a), was identified as a particularly large alumina inclusion. It was large enough to be visible by RLM when making the microhardness grid. Upon imaging in the SEM, it was obvious that the inclusion was so large that the electron beam could not fully penetrate it. This resulted in significant charging which was observed as the bright region on the centre of the inclusion in the micrograph.

Although Intermetallic #4 also appeared to be a mixed phase alumina inclusion, when it was imaged and analysed using a 15 keV electron beam, the beam envelope was able to fully penetrate it and alleviate charging, as observed by the clear contrast on the inclusion surface in Figure 6.30 (a). While it was known that charging of the inclusion would cause issue with analysis by AES and SAM it was decided to include the inclusion in the selection of intermetallics for further study as the large inclusions produced a unique corrosion environment. Cracks were observed at the inclusion/matrix interface for all of the large alumina inclusions. This is seen in Figure 6.67 (a). These cracks could provide a suitable region for crevice corrosion. In addition to the cracks other precipitates are observed at the inclusion/matrix interface. These are likely to have nucleated at the surface of the inclusions during hot pressing and aging of the beryllium metal. The additional nucleated material is observed on the majority of the large ceramic inclusions.
Initially it was thought that these large ceramic inclusions were an artifact of the polishing/lapping processes that these particular beryllium specimens had undergone prior to receiving them at the University. However, there is some evidence to suggest that this is not the case. Observed in the phase analysis of Intermetallic #8 were regions of additional material that appeared at the interface between the large inclusions and the beryllium matrix. In this case these are: elemental silicon on the top edge of the inclusion and an AlFeBe$_4$ type precipitate along the bottom edge. These materials are often seen at the interface of these types of inclusions and as the AlFeBe$_4$ is a precipitate from aging and not a inclusion produced from an impurity in the feedstock powder it is unlikely to track the interface of a particle so well if the particle was embedded in the surface as part of a post production polishing step.

The AES spectra collected from the centre of Intermetallic #8 are shown in Figure 6.68. These were collected using the analysis procedure for insulating samples described in Chapter 5. The survey spectrum (a) shows that the main elements present at the surface appear to be beryllium, aluminium and oxygen. A trace of silicon is present and appears to be in elemental form (b). The high resolution beryllium spectrum (c) shows the surface to consist of beryllium oxide. No metallic peak component is observed. Although the spectrum does reveal some sample charging as the peaks are shifted ~7 eV lower in kinetic energy. The high resolution Al KLL appears to show peaks for aluminium oxide and aluminium metal in similar concentrations. It is possible that this is a consequence of differential charging but the peak separation ~7 eV matches with the expected value for metal and oxide peaks.
Figure 6.68 AES spectra collected from the surface of the intermetallic prior to corrosion. (a) Survey spectrum, (b) high resolution Si KLL spectrum, (c) high resolution beryllium Auger and (d) high resolution Al KLL spectrum.

An EDX spectrum collected from the same position as the AES spectrum is shown in Figure 6.69. The spectrum shows intense Al Kα and O Kα peaks together with a weaker Si Kα peak and a particularly weak Fe Lα peak. Quantification from the spectrum is shown in Table 6.11. The quantification shows that the inclusion composition is consistent with an alumina particle with a small amount of silica also present.

Table 6.11 Quantification from Intermetallic #8, normalised to 100%

<table>
<thead>
<tr>
<th>Composition</th>
<th>Be</th>
<th>C</th>
<th>O</th>
<th>Al</th>
<th>Si</th>
<th>Fe</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intermetallic</td>
<td>-</td>
<td>0.6</td>
<td>49.3</td>
<td>43.4</td>
<td>4.0</td>
<td>2.6</td>
<td>0.1</td>
</tr>
</tbody>
</table>
6.4.9.2 Analysis as a function of time

Following each corrosion step AES and EDX point spectra were acquired together with an SEM micrograph of the surface. Spectra were not collected from the intermetallic after 64 hours and 128 hours. Figure 6.70 (a-j) shows the SEM micrographs collected from Intermetallic #8 after each corrosion step from time zero (a) to 128 hours (j). The difference in the brightness of the main body of the inclusion between the micrographs collected from zero to 4 hours and the other micrographs was that the secondary electron detector bias was turned off to try and compensate for the charging surface of the inclusion to make imaging easier. This was not a compositional change at the surface.

![Figure 6.70 SEM micrographs of Intermetallic #8 as a function of immersion time in NaCl. (a) Initial, (b) 15 min, (c) 45 min, (d) 2 hours, (e) 4 hours, (f) 8 hours, (g) 16 hours, (h) 32 hours, (i) 64 hours and (j) 128 hours.](image)
The micrographs reveal little change to the bulk of the intermetallic throughout the investigation. However, some small changes are observed on the top edge associated with the crack with the interface. To highlight these changes a series of higher magnification micrographs are shown in Figure 6.71. Apart from the changes highlighted in these micrographs no other changes were observed around the intermetallic. The micrographs show the development of small corrosive pits from small crevices (a + b) at the interface between the particle and the matrix, after 8 hours of immersion (c). These pits became covered with corrosion products after 16 hours (d) and showed little change in their structure and appearance for the remainder of the investigation.

![Figure 6.71](image.png)

Figure 6.71 Higher magnification SEM micrographs of the top region of Intermetallic #8 after different immersion times. (a) initial time, (b) 4 hours, (c) 8 hours, (d) 16 hours, (e) 64 hours and (f) 128 hours. The red arrows denote the areas of interest and the red points show the points at which EDX spectra were acquired.

To help determine the corrosion process EDX spectra were acquired from the points highlighted by the numbered red points in Figure 6.71 (f) and the spectra are shown in Figure 6.72. Points 1 + 3 are collected from the centre of the corrosion products which overlap the position of the crack. Points 2 + 4 are from nearby matrix and Point 5 is from the centre of the inclusion. Quantification was performed on the EDX spectra and this is shown in Table 6.12. The spectra from the nearby matrix are consistent with bulk beryllium with the addition of some signal from the nearby inclusion increasing the apparent intensity of the Al Ka and the Si Ka peaks. No chlorine is observed in the spectra collected from these points. The spectra collected from the two pit regions Points 1 and 3 show the presence of aluminium, silicon, oxygen and small amounts of iron and chlorine. The presence of chlorine indicates anodic attack of the matrix at this region. The aluminium and silicon in the spectrum and the quantification show that some of the analysis volume
overlaps with the inclusions, although this is expected because of the position of the beam. The large
corrosion of oxygen is out of balance with the other elements which could make up oxides, this shows
that the missing signal is beryllium. The signal from which has been attenuated by the corrosion products
and so the x-rays have not reached the detector. The spectrum and the quantification from Point 5 is
consistent with the spectrum collected from the centre of the intermetallic at time zero

\[
\text{Figure 6.72 EDX spectra from the points highlighted in Figure 6.71.}
\]

Table 6.12 Quantification of the EDX spectra collected from the five points, normalised to 100%

<table>
<thead>
<tr>
<th>Position / Composition</th>
<th>Be</th>
<th>C</th>
<th>O</th>
<th>Al</th>
<th>Si</th>
<th>Fe</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point 1</td>
<td>-</td>
<td>2.3</td>
<td>77.7</td>
<td>13.7</td>
<td>4.7</td>
<td>0.2</td>
<td>1.3</td>
</tr>
<tr>
<td>Point 2</td>
<td>40.0</td>
<td>2.8</td>
<td>37.9</td>
<td>17.2</td>
<td>1.6</td>
<td>0.6</td>
<td>ND</td>
</tr>
<tr>
<td>Point 3</td>
<td>-</td>
<td>1.9</td>
<td>72.4</td>
<td>20.1</td>
<td>4.0</td>
<td>0.3</td>
<td>1.2</td>
</tr>
<tr>
<td>Point 4</td>
<td>34.6</td>
<td>3.7</td>
<td>48.7</td>
<td>9.7</td>
<td>2.6</td>
<td>0.7</td>
<td>ND</td>
</tr>
<tr>
<td>Point 5</td>
<td>-</td>
<td>2.5</td>
<td>48.6</td>
<td>41.6</td>
<td>4.7</td>
<td>2.3</td>
<td>0.2</td>
</tr>
</tbody>
</table>

In addition to the point spectra from the corrosion features, an EDX map was acquired from the intermetallic
after 32 hours. This is shown in Figure 6.73. The maps were all processed using net counts. The most
noticeable change from the initial phase map that was acquired from the same region is the presence of
chlorine and additional oxygen associated with the corrosion at the top right of the intermetallic. The
chlorine map highlights that chlorine is generally absent on the intermetallic itself and is concentrated at the
site of the small pit observed in Figure 6.71 (c).
AES spectra were also collected from Points 1 and 3, these are shown in Figure 6.74. The survey spectra (a) show that both regions only show the presence of beryllium and oxygen at the surface while the high resolution beryllium Auger (b) shows the material to consist of oxide and metal peak components. This has the same spectral features as the material covering the surface of many of the previously investigated intermetallics after 16 hours of immersion.

6.4.11 Additional inclusion

Following 4 hours of immersion, it was observed that significant carbon contamination had built up on the surface of the samples. This contamination, resulted in the pyrolysed carbon rapidly accumulating on the surface of the inclusions, causing complete attenuation of the surface Auger electrons such that only carbon was observed in the survey spectra. Therefore, it was decided that because AES was no longer viable, to remove the sample from the glovebox to perform a brief UV-Ozone clean to remove the carbon. At this point the opportunity was taken to examine the surface using RLM. Although no signs of active pitting were observed anywhere on the sample including around any of the intermetallics that were being studied, a number of interference patterns were observed which were associated with various large inclusions. A
number of these were observed and one was located within the pre-marked grid and so it was included in further analysis. Figure 6.75 shows an RLM image together with a SEM micrograph the inclusions which showed an interference pattern in RLM. The interference patterns were associated with changes in the surface morphology and indicated an active process occurring at the surface. In (a) the bottom of the inclusion showed a pattern, this was associated with some deposited material near a crevice, as highlighted in (b). A crack is observed at this interface, as was the case for Intermetallic #8.

Figure 6.75 RLM image (a) and SEM micrograph (b) of an inclusion with an associated interference pattern. The red arrows highlight the position where the patterns were observed.

Phase analysis was performed on the EDX maps collected from the inclusion after 4 hours and are shown, together with the SEM micrograph of the region are in Figure 6.76. They show that the inclusion is homogeneous except for two small regions of beryllium rich material (b). These are observed as low intensity regions in the map of the inclusion (d). AlFeBe₄ precipitates are observed around most of the interface with the matrix (c) and a small silicon inclusion is also observed attached to the inclusion (e).

Figure 6.76 Phase analysis of the EDX maps collected using the MICROLAB from the additional intermetallic. (a) SEM micrograph of the intermetallic, (b) beryllium metal matrix, (c) AlFeBe₄ precipitates at the interface, (d) Al₂O₃ inclusion and (e) silicon inclusion at the interface.

In addition to the EDX map, AES spectra were collected from the surface of the inclusion. These are shown in Figure 6.77. The survey spectrum (a) shows that only Be KLL and O KLL Auger transitions are present. Indicating that the surface does not contain any of the elements that are present in the bulk of the particle.
The high resolution beryllium spectrum (b) shows the peak shape believed to represent beryllium hydroxide. The presence of some beryllium hydroxide on the surface of the inclusion fits with the observation that corrosion product material is observed on the matrix surrounding the inclusion after 4 hours of immersion in the SEM micrograph.

![Figure 6.77 AES spectra collected from the surface of the inclusion after 4 hours immersion. (a) survey spectrum, (b) high resolution beryllium Auger spectrum.](image)

SEM micrographs were collected after each immersion step following the initial micrograph collected after 4 hours. The micrographs are shown in Figure 6.78. They show the progressive deposition of corrosion products at the interface between the particle and the matrix. The initial material appears to be deposited as small clusters in a circular halo around the inclusion (a-c). The volume of deposited material increases significantly between 16 hours (c) and 32 hours (d) and then again after 64 hours (e). The amount of material appears to be fairly unchanged between 64 hours and 128 hours, possibly indicating some passivity of the region.

![Figure 6.78 SEM micrographs of an additional intermetallic studied after 4 hours prior immersion in NaCl (a) 4 hours, (b) 8 hours, (c) 16 hours, (d) 32 hours, (e) 64 hours and (f) 128 hours.](image)
To help determine the corrosion process that was occurring, EDX spectra were acquired from the points highlighted by numbered red points in Figure 6.79. The spectra together with spectrum acquired from the centre of the inclusion after 4 hours are shown in Figure 6.80. Quantification of each spectrum is shown in Table 6.13. They show that the spectrum collected from the centre of the inclusion matches that collected initially from the same spot with no change in the resulting quantification. Points 2 and 4 from the crevice region and Point 3 from the corrosion products all show the presence of small amounts of chlorine. This indicates the anodic attack of the matrix in this region.

Figure 6.79 SEM micrograph of the inclusion after 32 hours of immersion. The highlighted points denote the positions from which EDX spectra were acquired.

The high concentration of oxygen in the spectra shows the presence of beryllium containing corrosion products because insufficient alternative counter ions are present to produce oxides or hydroxides consistent with the quantification. The spectrum from Point 5 and the centre of the inclusion Point 1 do not show any chlorine, showing that the matrix around the inclusion and the inclusion itself are not being corrosively attacked.

Figure 6.80 EDX spectra from the points highlighted in Figure 6.79.
### Table 6.13 Quantification from the EDX spectra collected from the additional inclusion, normalised to 100%

<table>
<thead>
<tr>
<th>Position / Composition</th>
<th>Be</th>
<th>C</th>
<th>O</th>
<th>Al</th>
<th>Si</th>
<th>Fe</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>3.0</td>
<td>51.7</td>
<td>40.3</td>
<td>3.9</td>
<td>1.2</td>
<td>ND</td>
</tr>
<tr>
<td>Point 1</td>
<td>-</td>
<td>1.3</td>
<td>54.4</td>
<td>39.0</td>
<td>4.5</td>
<td>0.8</td>
<td>ND</td>
</tr>
<tr>
<td>Point 2</td>
<td>-</td>
<td>2.4</td>
<td>91.4</td>
<td>2.7</td>
<td>3.0</td>
<td>ND</td>
<td>0.5</td>
</tr>
<tr>
<td>Point 3</td>
<td>-</td>
<td>1.4</td>
<td>97.3</td>
<td>0.4</td>
<td>0.3</td>
<td>ND</td>
<td>0.7</td>
</tr>
<tr>
<td>Point 4</td>
<td>-</td>
<td>2.1</td>
<td>95.1</td>
<td>1.6</td>
<td>0.4</td>
<td>ND</td>
<td>0.8</td>
</tr>
<tr>
<td>Point 5</td>
<td>43.5</td>
<td>0.8</td>
<td>55.4</td>
<td>ND</td>
<td>0.4</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

In addition to the point spectra, EDX maps were acquired from the inclusion after 32 hours are shown in Figure 6.81. The maps were processed using net counts. The maps show the loss of the well-defined edge of the inclusion with the matrix. This is caused by the deposition of beryllium hydroxide corrosion products. This is noticeable by the intense oxygen rich material shown in the oxygen map (d). It is apparent from this map that the products are associated with and are most densely deposited around the inclusion/matrix interface. The aluminium and silicon maps (b and c) show the presence of the inclusion underneath the corrosion products. They are not present on the local matrix showing that the inclusion is not dissolved during the corrosion process. The chlorine map (e) shows an increase in the concentration of chlorine at the crevice, around the inclusion, with an absence of chlorine from the region of the inclusion. This map is consistent with the chlorine map acquired from Intermetallic #4 after 64 hours. This appeared to show evidence for crevice corrosion at the particle/matrix interface.

![Figure 6.81 EDX maps from the additional inclusion, after 64 hours of immersion. (a) SEM micrograph, (b) aluminium, (c) silicon, (d) oxygen and (e) chlorine.](image)

### 6.4.12 Diagnosis of galvanic activity by cation deposition

To estimate the cathodic current density and determine if the intermetallics were acting as cathodes to the surrounding alloy, the sample was sequentially immersed in solutions of magnesium chloride with concentrations of 0.01 M, 0.1 M, 0.5 M and 5.0 M for 30 minutes. Despite beryllium hydroxide being more insoluble than magnesium hydroxide, the use of magnesium chloride solutions to deposit magnesium hydroxide was desired because it is difficult to differentiate beryllium hydroxide from beryllium oxide.
Therefore, for the unambiguous identification of cathodic areas, a material not present in beryllium was desired. The appearance of magnesium in the AES spectra would positively identify a cathodic surface region. Table 6.14 shows the solutions used in this investigation. The solutions were prepared from analytical grade hydrated magnesium chloride MgCl$_2$(H$_2$O)$_6$ (203.31 g mol$^{-1}$) and ultra pure DDI water. The solubility of magnesium chloride in room temperature water is ~5.3 M and so the solid in the 5 M solution required significant agitation in an ultrasonic cleaner to fully dissolve as it was so close to a saturated solution.

**Table 6.14 Values used for the magnesium chloride solutions**

<table>
<thead>
<tr>
<th>Concentration (mol dm$^{-3}$)</th>
<th>Volume (ml)</th>
<th>Moles</th>
<th>Required mass MgCl$_2$(H$_2$O)$_6$ (g)</th>
<th>Actual mass used (g)</th>
<th>Actual concentration (mol dm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>50</td>
<td>0.0005</td>
<td>0.10166</td>
<td>0.1033</td>
<td>0.010</td>
</tr>
<tr>
<td>0.1</td>
<td>50</td>
<td>0.005</td>
<td>1.01655</td>
<td>1.035</td>
<td>0.102</td>
</tr>
<tr>
<td>0.5</td>
<td>50</td>
<td>0.025</td>
<td>5.08275</td>
<td>5.0433</td>
<td>0.496</td>
</tr>
<tr>
<td>5.0</td>
<td>50</td>
<td>0.25</td>
<td>50.8275</td>
<td>50.8105</td>
<td>4.998</td>
</tr>
</tbody>
</table>

This was performed on another beryllium sample that was not used for the main corrosion investigation. Explained in Chapter 4, was the theory surrounding the test, the cathodic regions of the sample become plated with magnesium hydroxide deposits when exposed to a critical concentration of magnesium chloride solution. Exposing the samples to increasing concentrations of magnesium hydroxide enabled the bracketing of the critical concentration at which magnesium hydroxide precipitated onto the cathodic area and therefore bracket the cathodic current density of the second phase particles. As was the case for a copper rich intermetallic studied in Chapter 4. In the case of a cathodic matrix it acts to mark the surface as cathodic but does not enable the calculation of the cathodic current density as the area of the matrix that acts cathodically is difficult to isolate.

Survey spectra and high resolution spectra were collected from the surface of a range of second phase particles that matched the compositions of the particles studied in this chapter, in addition to beryllium nitride inclusions and CdZr intermetallics. Analysis points were also placed on the surrounding matrix in case the particles were anodic with a cathodic local matrix. The results from the investigation are shown in Table 6.15.

**Table 6.15 Results from the magnesium cation precipitation test**

<table>
<thead>
<tr>
<th>Second phase particle type</th>
<th>Diameter of inclusion (μm)</th>
<th>Concentration at which Mg observed (mol dm$^{-3}$)</th>
<th>Position of Mg on surface (on/off inclusion)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlFeBe$_2$</td>
<td>2.3</td>
<td>1.4</td>
<td>Not observed</td>
</tr>
<tr>
<td>Ti$_3$Si</td>
<td>1.6</td>
<td>1.5</td>
<td>Not observed</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>7.0</td>
<td>7.5</td>
<td>Not observed</td>
</tr>
<tr>
<td>Si</td>
<td>2.8</td>
<td>1.3</td>
<td>Not observed</td>
</tr>
<tr>
<td>Cd + Zr</td>
<td>1.9</td>
<td>-</td>
<td>Not observed</td>
</tr>
<tr>
<td>Be$_3$N$_2$</td>
<td>4.3</td>
<td>-</td>
<td>Not observed</td>
</tr>
</tbody>
</table>

No trace of magnesium was observed in the survey or high resolution spectra collected from the particles or the matrix surrounding them within the tested concentration range. This shows that little galvanic activity is present between these particle types and the matrix. The radius of each particle was used to calculate the cathodic current density range over which they are not cathodically active, the results are shown in Table
6.16. The absence of magnesium on the local matrix also shows that if the particles are anodic with the adjacent matrix acting as the cathode then the activity is extremely low. It is not possible to calculate a cathodic density of the matrix because the area over which it is active is unknown.

Table 6.16 Calculated cathodic current density range over which various second phase particles are not active

<table>
<thead>
<tr>
<th>Second phase particle type</th>
<th>Cathodic current density range (mA m^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Max</td>
</tr>
<tr>
<td>AlFeBe_4</td>
<td>15.23</td>
</tr>
<tr>
<td>Ti_3Si</td>
<td>14.22</td>
</tr>
<tr>
<td>Al_2O_3</td>
<td>3.05</td>
</tr>
<tr>
<td>Si</td>
<td>16.41</td>
</tr>
<tr>
<td>Cd + Zr</td>
<td>11.22</td>
</tr>
<tr>
<td>Be_3N_2</td>
<td>4.96</td>
</tr>
</tbody>
</table>

6.5 Discussion

6.5.1 General discussion and observations

The first evidence for the onset of corrosion was in RLM images collected after 4 hours. No signs of active pits were observed on the surface at this time but interference patterns were observed at the interface between inclusions and the matrix for a number of large inclusions. These were apparent even at a fairly low magnification. An RLM image of the additional inclusion is included which shows this effect. They were the result of material deposition at the periphery of the inclusion on the matrix. This material causes the refraction of light at the surface as if a thin film is present resulting in the interference pattern. This effect enabled the study of an additional inclusion that were not part of the original set selected for analysis. This inclusion was found to be active, showing crevice corrosion.

Significant localised corrosion was observed within the microhardness indentation grid. RLM images of the grid prior to corrosion and after 128 hours of immersion are shown in Figure 6.82 (a) and (b) respectively. The surface was heavily pitted at localised sites within the grid, a number of the pits were visible to the naked eye. Only one pit was observed to be present at the site of a microhardness indentation suggesting that their influence on the corrosion process was minimal.

Figure 6.82 RLM images of the microhardness indent grid (a) before the corrosion investigation and (b) after 128 hours of immersion in 0.1 M NaCl solution.
The ratios of Al:Fe in the AlFeBe₄ precipitates were not found to be 1:1 as expected. In a one of the precipitates (Intermetallic #1) the ratio is much closer to 2:1, with a 20 at.% excess of aluminium observed. Some of this difference may be a consequence of the error introduced during the quantification procedure, however, for Intermetallic #5 an excess of iron was observed suggesting that the quantification may be correct. It has previously been suggested that other transition metal elements could substitute into the AlFeBe₄ lattice in place of iron [25]. Chromium and manganese are observed to be present in a number of the AlFeBe₄ precipitates at various concentrations, as shown in the summary Table 6.1. Both of these atoms have smaller radii than iron and may be able to substitute into the crystal structure. It should be noted that the concentration of manganese is higher than expected because the Mn Kα x-ray line overlaps with the Cr Kβ line. Even using the concentrations of chromium and manganese as they are in the composition table the aluminium is still present in a significant excess.

A third explanation for the excess of aluminium, present in the inclusions, comes from a recently published study in combination with work previously mentioned in the literature review [109]. These have shown that additional crystal structures can form in the Al-Fe-Be system including (Al, Fe)Be₅, Al₂FeBe₃ and (Al, Fe)Be₂. In these structures the aluminium and iron are interchangeable and can substitute for one another. The presence of these additional phases, which would not be unambiguously detectable in the samples by EDX or AES would explain the observed excess in aluminium.

A large number of alumina inclusions were observed when the surface was examined in the SEM. Their identification was made simple as the particles all caused significant charging and appeared bright against the beryllium matrix. The particles usually showed precipitates of silicon and AlFeBe₄ at the matrix interface, in addition to a crack at the interface with the matrix.

These large alumina particles are most likely present as the result of wear on the milling media used in the ball milling process for the production of fine grained beryllium. All commercially available milling media is sold with a stated wear rate, which can be as high as 0.1 wt.% per hour of milling. The purity of alumina based media is typically between 85-95 wt.% Al₂O₃, with additives of silicon dioxide, magnesium oxide and calcium oxide. These are included to improve the wear properties of the milling media and as processing aids [110]. The only other process that beryllium undergoes from extraction to the final analysed piece that could introduce such particles the metallographic preparation processes of grinding and polishing. However, the large size of the inclusions, > 20 μm in diameter, corresponds to an unusually large grit size that would not typically be used for these final sample preparation stages.

Based upon the observations made from the individual intermetallics discussed in the following sections the beryllium oxide and large alumina particles are present in the feedstock beryllium powder prior to hot pressing, as surface oxide on beryllium and contamination particles respectively. Silicon precipitates during this process and appears to nucleate from the oxide and alumina inclusions. Then the overaged AlFeBe₄ precipitate can nucleate from any one of these second phase particles. The titanium-silicon particles also appear to be present in the metal prior to the formation of the AlFeBe₄ precipitate.
6.5.2 Intermetallic #1

The first intermetallic that was studied was a particularly large AlFeBe$_4$ precipitate with a damaged region from the polishing process. From the initial EDX results the particle contained an excess of aluminium compared to the ideal ratio of 1:1 for aluminium to iron. The surface oxide layer as found by AES was predominately beryllium oxide with the possible incorporation of some aluminium oxide.

The intermetallic did not appear to undergo any significant changes until after 8 hours of immersion, at which point the onset of corrosion product deposition was observed in a halo around the particle. More corrosion products are then deposited in this halo after 16 hours. Eventually so much material is deposited around the particle that it forms a dome which fully envelops the particle and a portion of the matrix surrounding it. The EDX maps collected after 64 hours of immersion still show a definite region of aluminium and iron enrichment in the centre of the map consistent with the particle. Examination of the EDX spectra from the dome and the EDX maps shows that it does not contain aluminium or iron which make up the intermetallic particle but contains oxygen and traces of chlorine. This suggests it is formed of beryllium oxide/hydroxide as a result of precipitation from solution at a critical cathodic potential or pH.

The absence of any material depositing onto the particle itself, as shown by the absence of material in the SEM micrographs and the absence of an oxygen rich region on the intermetallic suggested that the particle was behaving as a local anode. Additionally, the absence of aluminium, silicon, iron, chromium or manganese in the corrosion products, which were the particle constituents besides beryllium, suggests that the anodic reaction involves the dealloying of the most anodic particle element, beryllium. The dealloying of beryllium from the particle would result in the behaviour observed in the ring of material and the apparent anodic behaviour.

A trace amount of copper was observed to deposit onto the particle surface during the investigation. This process has been observed in aluminium alloys for anodic particles which undergo a dealloying process of their most anodic constituent element. The copper is deposited onto the particle with the eventual generation of a nobler particle, by the action of the copper and the remaining noble elements in the particle becoming enriched by the loss of the anodic constituent.

Previous work synthesising bulk forms of this precipitate for electrochemical assessment has been performed which suggests that it will behave as an anode under neutral conditions. However this study was performed using a S-200D grade beryllium matrix [48]. This beryllium contains significantly more metallic impurities. Therefore, it is reasonable to conclude that the bulk beryllium used in the study might be more cathodic than the lower metal content S-65 grade beryllium. Additionally, the use of bulk intermetallic samples as an analogue to real intermetallics in a material is not typically recommended as a method for extrapolating true behavioural information of intermetallics in their usual host material [111]. This is because it is difficult to ensure that the bulk material actually represents the intermetallics composition and homogeneity. These bulk
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materials also contain defects and grain boundaries which may not be representative of micrometer sized second phase particles.

6.5.3 Intermetallic #2

The second intermetallic was a rectangular AlFeBe₄ precipitate. The intermetallic was particularly unusual for an AlFeBe₄ precipitate because it was particularly regular in shape unlike the majority of this intermetallic type, which were typically long and thin as highlighted in Figure 6.83.

![Figure 6.83 SEM micrograph to highlight the typical geometry of AlFeBe₄ precipitates.](image)

The EDX phase analysis showed the particle to be homogeneous and that it had a larger subsurface volume than was immediately apparent from the SEM micrographs. The EDX point analysis showed the particle to be similar in composition to the first intermetallic. The main difference was a notable reduction in the concentration of chromium and manganese with a corresponding increase in the concentration of iron. The AES point spectra from the initial surface showed that the surface of the particle was covered with an oxide containing mainly beryllium oxide and a trace of aluminium oxide. It is not possible to extract chemical information from the Fe LMM and so the presence of iron in the oxide is unknown.

The AES point spectra collected as a function of time showed the gradual reduction in the intensity of the Al KLL and the Fe LMM peaks. The intensity of the beryllium Auger and the ratio between the metallic and oxide peak components did not appear to change. The reduction in the aluminium and iron Auger intensity would suggest that the either they were dissolved from the surface of the intermetallic or that a layer of general corrosion products on the surface was attenuating their signal. The explanation of a thin layer of material seems the more likely, as the presence of material spread across the surface was observed in the SEM micrographs of the intermetallic.

The EDX spectra that were collected as a function of time from the centre of the intermetallic showed no change to the bulk. All of the peaks that were observed in the initial spectrum were still observed in the spectrum following 32 hours of immersion with the same peak intensities.
Intermetallic #2 was not found to have an active role in the corrosion process. No evidence for galvanic activity resulting in the precipitate being anodic or cathodic was observed. No corrosion products were deposited onto the surface and no attack of the adjacent matrix was observed. Additionally, no evidence was observed for crevice corrosion at the particle/matrix interface. The difference in the observed behaviour between Intermetallic #1 and Intermetallic #2 did not appear to be caused by a difference in particle size as both were \( \sim 7 \, \mu\text{m} \). Their compositions varied slightly with Intermetallic #1 containing less iron but more chromium and manganese than Intermetallic #2. However, the most noticeable difference between the two particles was the mechanical damage at the surface of the first while the second remained smooth to the polished surface.

### 6.5.4 Intermetallic #3

The third intermetallic that was studied was a large AlFeBe\(_4\) precipitate with a complex geometry, this contrasted well with the simple geometry of Intermetallic #2. EDX phase analysis showed the majority of the inclusion to be homogeneous except for a small titanium-silicon inclusion associated with it. Quantification of the EDX spectrum showed the composition to be almost identical to that of Intermetallic #2, showing the same compositional differences as it did to Intermetallic #1, containing more iron but less chromium and manganese. The EDX spectra collected as a function of time showed little change throughout the investigation. The most noticeable difference was the appearance of an intense C K\(\alpha\) peak in the spectrum collected after 4 hours. This was caused by the previously mentioned thick layer of carbon contamination on the surface after this immersion step. Although the sample was UV-Ozone cleaned a significant amount of carbon was still present at the spot where EDX was performed resulting in the carbon peak still being observed in the EDX spectra.

The AES spectra collected from the initial surface showed weaker Fe LMM and Al KLL peaks in the survey spectrum compared to the survey spectrum collected from Intermetallic #2. This suggested that a thicker layer of beryllium oxide covered the intermetallic. This was confirmed by the appearance of the beryllium Auger region which showed a more intense oxide component in the spectrum collected from the intermetallic. The high resolution spectra indicated that the oxide layer present on the intermetallic was mainly composed of beryllium oxide with a trace of aluminium oxide.

The spectra collected as a function of time highlight the deposition of carbon contamination following the 4 hour immersion with the appearance of an intense C KLL peak, this material almost completely attenuates the electrons from the high resolution spectra collected at that time. The spectra showed the gradual reduction in the intensity of the Al KLL and the Fe LMM peaks. This was consistent with the behaviour observed for the other intermetallics and is thought to be caused by the gradual build-up of a thin layer of corrosion products over the entire sample surface from the rinsing steps used to remove excess electrolyte after the corrosion step.
Some slight changes in the appearance of the surface were observed following 4 hours of immersion. These were a dark halo all around the inclusion and small circular dark patches on the inclusion itself. This was the result of carbon deposition under the electron beam and not a corrosion phenomenon.

The SAM maps that were acquired from the initial surface showed that the exposed surface of the particle was slightly smaller than initially believed because of the glow of the subsurface particle material. The maps only showed the regions of the particle that were actually exposed at the metal surface.

The intermetallic appeared to show no signs of an active role in the corrosion process. No evidence for galvanic activity resulting from the particle being anodic or cathodic was observed. Corrosion products were not observed to deposit on or around the particle and no attack of the matrix was observed. Additionally, no evidence for crevice corrosion at the interface between the precipitate and the matrix was observed. The absence of any corrosive activity associated with Intermetallic #2 and Intermetallic #3, despite being of similar or larger size than Intermetallic #1 and of similar composition, suggests the morphology of the AlFeBe₄ precipitate does not appear to play a role in the propensity for the particle to cause corrosion. This suggests that the more dominant precursor for corrosion the presence of damage to the surface of the particle.

6.5.5 Intermetallic #4

Upon initial examination of the EDX spectra and quantification of the spectra this particle was thought to be an Al₂O₃ inclusion, much like Intermetallic #8 because the particle contained oxygen and aluminium. However, closer inspection of the EDX data showed that quantification was not consistent with the alumina particles observed in the metal. The O Kα peak intensity was considerably greater than the Al Kα peak and the resulting oxygen concentration was ~75%. The only stable oxide of aluminium is Al₂O₃ with a 1:1.5 ratio but the inclusion has a ~4.1 ratio so it cannot be all aluminium oxide. Based upon the quantification it is possible that the particle contained beryllium hydroxide/oxide together with alumina. The beryllium hydroxide could have been generated by the hydrolysis of the carbide. The presence of a significant amount of subsurface carbon was observed in the initial EDX maps of the particle. Carbon was absent at the surface as none was observed in the initial AES spectra. However, this is expected for beryllium carbide. As discussed in Chapter 5, the acquisition of a carbon Auger transition from a carbide inclusion required significant argon ion etching and the mechanical scribing of the surface in vacuum.

The formation of a halo or ring of corrosion products surrounding the inclusion at a constant distance away from the particle is indicative of an electrochemical process and is very similar to the behaviour observed for Intermetallic #1. However, the initial material at the rim of the intermetallic is similar to the behaviour of the additionally studied inclusion, with the deposition of a small amount of material of the matrix immediately adjacent to the particle. The ring of corrosion products takes longer to form for this intermetallic taking 16-32 hours compared to 8 hours for Intermetallic #1, suggesting a lower activity.

The particle appears to display a mixture of galvanic activity combined with crevice activity. It is possible that the dealloying or dissolution of beryllium from the particle gradually reduces the anodic potential.
Eventually reaching the point where the particle is not active with respect to the matrix and contains only inactive alumina and silica constituents. These are then unable to continue the galvanic couple with the matrix but do form a crevice with the matrix. As such, corrosion continues at the particle/matrix interface resulting in the deposition of corrosion products at the crevice mouth. This switch in behaviour explains why no more material deposits in the outer ring of material between 32 hours and 128 hours but material is deposited at the interface of the particle during this time. As for Intermetallic #1 no corrosion products are observed to deposit on the surface of the particle.

6.5.6 Intermetallic #5

The fifth intermetallic was a mixed phase silicon and AlFeBe₄ particle. It was often observed that AlFeBe₄ precipitates had nucleated from elemental silicon inclusions in the beryllium. Figure 6.84 shows an example of two precipitates which had nucleated from a silicon particle.

The SEM micrographs, EDX phase analysis, and AES maps showed a well-defined interface between the two phases. The EDX point analysis showed the intermetallic to have a composition unlike any of the previously investigated AlFeBe₄ precipitates. Instead of an excess of aluminium the intermetallic had a slight excess of iron ~7 at.% compared to the aluminium. This excess would be reduced to almost zero if silicon was also present in the AlFeBe₄ structure in place of aluminium. However, as was described in the literature review, attempts to produce a silicon substituted phase of AlFeBe₄ resulted in failure and it was concluded that the phase does not form [25]. As such it is likely that the excess iron is the result of the mixed crystal structures, in which iron is substituted in place of aluminium in the (Al, Fe)Be₄ structure.

The AES spectra collected from the AlFe side prior to corrosion showed the surface to consist of beryllium oxide with a trace of aluminium oxide. Unlike the other AlFeBe₄ precipitates the spectrum also showed a significant amount of elemental silicon to be present at the surface of the inclusion. This was not in the form of oxide. The AES spectra collected from the silicon side showed the surface to consist of silicon with a particularly thin oxide layer. This is shown by the small oxide components in the surface sensitive Si LMM Auger transition.
The AES spectra collected as a function of time showed a similar relationship as observed for Intermetallics #2 and #3, with the progressive reduction in the intensity of the Al KLL, Fe LMM and Si KLL Auger peaks, while the beryllium Auger transition appeared to show little change. The appearance of the beryllium Auger region in the spectrum acquired from the silicon side as a function of time adds confidence to the belief that a thin film of beryllium corrosion products was dispersed over the entire sample surface which attenuated the electrons from the elements present in the intermetallics. Beryllium is not present in the silicon inclusions because beryllium does not form a compound with silicon at any concentration [112]. Therefore, silicon could not be selectively dissolved from the surface of the intermetallic to leave behind a surface rich in beryllium because no beryllium would be present in the particle initially.

The beryllium Auger transition showed metal and oxide components in the spectra from the silicon and AlFe sides of the intermetallic after 32 hours. This signal is from the thin film of corrosion products covering the entire sample surface. This conclusion would indicate that beryllium hydroxide has an Auger spectrum representative of a material with covalent and ionic bonding.

The only change that was observed in the EDX spectra from the AlFe side of the inclusion over the course of the investigation was a slight drop in the intensity of the Si Kα peak after 15 minutes. However this was a result of the position for analysis being located slightly further from the silicon side than the other analysis points. Apart from this, no other deviations from the initial spectrum were observed. The EDX spectra collected from the silicon side also showed no change over the course of the investigation. The small Al Kα peak that is observed is likely the result of some overlap of the primary electron beam scattering volume into the aluminium containing side of the inclusion. The slight variations in the intensity of the silicon peak are the result of changes in the live time of the spectra. The analysis of silicon results in an extremely high dead time > 90% for the EDX detector and so the acquisitions were stopped part way through to stop the spectrometer from collecting the single spectrum for 1 hour.

The AES, spectra, EDX spectra and SEM micrographs showed no significant evidence that the intermetallic was involved in galvanic corrosion. Additionally, no evidence was observed for crevice corrosion at the interface between the inclusion and the matrix.

6.5.7 Intermetallic #6
The sixth intermetallic was an elemental silicon inclusion. EDX phase analysis showed it to be homogeneous in composition. The initial AES spectra showed the surface of the particle to have a thin oxide layer. This was revealed by the small oxide peak components in the Si KLL Auger transition and the more surface sensitive Si LMM Auger transitions.

The EDX and AES spectra showed the same relationship was observed for Intermetallic #5. No change in the x-ray peak intensities in the EDX spectra was observed. Additionally, the AES spectra showed the gradual reduction in the intensity of the Si KLL peak and a shift in the appearance of the beryllium Auger region from entirely silicon envelope to a mixed beryllium metal and oxide peak envelope.
No evidence for galvanic activity associated with the particle was observed. No corrosion products were observed on the particle or on the matrix surrounding the particle. No accelerated corrosion of the adjacent matrix was observed. Additionally, no signs of crevice corrosion were observed at the interface between the inclusion and the matrix.

Based upon the observations from the silicon side of Intermetallic #5 and Intermetallic #6, in contrast to previous experimental investigations [23], elemental silicon inclusions do not appear to initiate pitting corrosion in beryllium.

6.5.8 Intermetallic #7

A number of titanium-silicon phases are present within the binary phase diagram. These include: TiSi$_2$, TiSi, Ti$_5$Si$_4$, Ti$_3$Si$_3$ and Ti$_4$Si. Of these binary phases, Ti$_3$Si most closely matches the composition as found by EDX. However, the WDX analysis performed in Chapter 5 on these inclusion types together with the metallic beryllium peak component in the beryllium Auger region, suggested that beryllium was present within the intermetallic. Thus, while it has been identified in this Chapter as Ti$_3$Si it is likely to be Be$_x$Ti$_{3y}$Si$_y$.

No information is available within the literature describing this ternary phase diagram or this inclusion type.

The behaviour of this particle closely followed that of the first intermetallic studied, which was an AlFeBe$_4$ precipitate. The intermetallic did not appear to undergo any significant changes until after 8 hours of immersion. To corrosion products were observed to deposit in a circle around the intermetallic. No products were observed on the intermetallic itself or on the matrix immediately adjacent to the particle. After 16 hours more corrosion products had deposited in the circle but again none were observed on the intermetallic or the matrix adjacent to it. This region where material was not deposited was smaller than that observed for Intermetallic #1, suggesting that the activity of the Ti$_3$Si intermetallic was lower. Between 16 hours and 32 hours of immersion enough material is deposited around the inclusion to form a dome of corrosion products. This dome completely covers the intermetallic from view and hinders analysis. Although, the EDX maps collected after 64 hours of immersion still show a definite region of titanium and silicon enrichment in the centre of the map consistent with the particle.

Examination of the EDX spectra from the dome and the EDX maps shows that it does not contain of aluminium or iron which make up the intermetallic particle but contains oxygen and traces of chlorine. This suggests it is formed of beryllium oxide/hydroxide as a result of precipitation of the beryllium ions from solution at a critical cathodic potential or pH.

The absence of any material depositing onto the particle itself, as shown by the lack of material in the SEM micrographs and the absence of an oxygen rich region on the intermetallic suggested that the particle was behaving as a local anode. Additionally, the absence of titanium or silicon in the corrosion products, which were the particle constituents besides beryllium, suggests that, as thought to occur for Intermetallic #1, the anodic reaction involves the dealloying of the most anodic particle element, beryllium. The dealloying of beryllium from the particle would result in the behaviour observed in the ring of material and the apparent
anodic behaviour. In addition to these observations, the test for cathodic activity around inclusions of the same composition did not show magnesium hydroxide deposition on the intermetallics.

As observed to occur on the first intermetallic a small amount of copper deposited onto the surface of the particle. The presence of copper together with a dealloyed intermetallic would eventually result in the intermetallic becoming nobler than the surrounding matrix. This would, in time, cause the particle to behave as a local cathode with the accelerated removal of the surrounding beryllium matrix. The copper is thought to have originated from trace impurities in the water used during the corrosion investigation or from the extremely low concentrations present in the metal. The presence of copper was determined during the automated EDX analysis routine described in Chapter 5.

Previous experimental investigations have shown a link between titanium or titanium silicon containing second phase particles \[15,48\]. Therefore, in agreement with these investigations, the phase believed to be \(\text{Ti}_3\text{Si} \) or \(\text{Be}_x\text{Ti}_3\text{Si} \) does have an active role in the corrosion of beryllium.

### 6.5.9 Intermetallic #8

The eighth intermetallic was a particularly large alumina inclusion. The inclusion showed precipitates of silicon and \(\text{AlFeBe}_4\) at the inclusion periphery, in addition to a crack at the interface with the matrix. EDX quantification of the inclusion was consistent with ceramic material that is typically used as mechanical milling material, containing a small amount of silica in addition to the alumina.

The inclusion did not show signs of activity until after 4 hours of immersion. At which point two small regions of corrosive attack were observed at the matrix/inclusion interface. Successive immersion after this initial attack showed the formation of voluminous beryllium hydroxide corrosion products at the interface. The material covering the small pits appeared to cap the active region that had formed because no further significant activity was observed from these two regions for the remainder of the investigation. EDX point spectra and x-ray maps revealed chlorine to be associated with these regions that was not associated with the matrix or the inclusion itself. The presence of chlorine at this region shows that localised anodic dissolution of matrix material was occurring. No corrosion products were observed on the particle surface. This is explained by the charging that was observed in the SEM micrographs. The particle being ceramic and non-conducting was not able to have an active role in the corrosion process other than to act as a crevice former. Being non-conductive the oxidation reaction at the pit mouth that occurs to balance the reduction of the matrix within the crevice cannot occur because the electrons from the reduction cannot tunnel through the particle to the particle surface to generate hydroxyl ions.

The activity was not associated with the entire crack and the side of the inclusion with the \(\text{AlFeBe}_4\) precipitate and did not appear to be associated with the attached silicon particle. It is possible given the observed behaviour of the \(\text{AlFeBe}_4\) precipitate, which appeared to be anodic, that the slight cathodic behaviour of the crevice mouth caused by an oxygen differential cell formation is countered and balanced by
the anodic activity of the precipitate. This would then result in zero potential difference at the pit mouth resulting in no driving force for the anodic dissolution of the subsurface material in the crevice.

### 6.5.10 Additional inclusion

The additional inclusion was a large homogeneous alumina particle. EDX showed the composition to be almost identical to Intermetallic #8, containing aluminium oxide and silicon, likely in the form of silicon dioxide, together with a trace of iron. The particle was again likely to be present as the result of wear from milling media used in the production of beryllium powder.

Chlorine was found to be present at the interface between the inclusion and the matrix and associated with the corrosion products deposited onto the matrix adjacent to the inclusion. No corrosion products were observed to deposit onto the inclusion itself. Additionally, no evidence for dissolution of the inclusion was observed.

The corrosion process associated with the inclusion was typical of micro crevice corrosion. This particle showed more severe corrosive activity than Intermetallic #8, despite both particles having similar compositions and morphologies. A possible explanation for the enhanced activity could be the size of the crevice mouth. The narrower the entrance to the crevice the lower the rate of oxygen diffusion into the crevice resulting in a greater potential difference between the crevice and the cathodic metal surface surrounding the inclusion, resulting in accelerated attack within the crevice. The crevice mouth of Intermetallic #8 could be larger resulting in slower corrosion compared to the additional inclusion. However, the crevice mouth could also be so small such that the corrosion products produced at the cathode which produced the voluminous material covering the pit formed a barrier between the crevice and the electrolyte. This material would prevent ionic diffusion from the anode to the cathode inhibiting the corrosion process for Intermetallic #8.

### 6.6 Instrumental aspects

#### 6.6.1 The choice of beam energy

During EDX analysis two problems were encountered. These were: blurring of the edges of the intermetallics and sample drift. These are both linked to each other. To minimise the chances of sample drift caused by mechanical drift of the stage over time, a high primary beam energy should be used in order to maximise excitation cross section for the peaks of interest. This increases the x-ray yield for a given analysis time. However, by increasing the primary beam energy from 10 keV which was used for Auger analysis to 15 keV, which is typical for EDX analysis, significant blurring of the intermetallic edges occurred. This blurring is likely the result of the particularly large interaction volume of the beam at this energy and the lack of attenuation of the x-rays from the intermetallic within the beryllium matrix.

The effect of the higher beam energy is shown for in Figure 6.85 for an intermetallic with a complex geometry. The figure shows the SEM micrograph (a) together with EDX maps collected with primary beam energies of 10 keV (b) and 15 keV (c). The geometry and intricate structure of the intermetallic is
considerably clearer in the 10 keV EDX map. The EDX map collected using the 15 keV beam energy shows little of the fine structure, with only the central region where the intermetallic was thickest outlined clearly.

Figure 6.85 SEM micrograph of an intermetallic of interest (a). EDX map of aluminium collected with 10 keV primary beam energy (b). EDX map of aluminium collected with 15 keV primary beam energy (c).

This led to the decision that the EDX maps would be collected with a 10 keV beam energy and that the analysis would be performed for longer than would otherwise be used for a 15 keV beam. A suitable balance was found at 5 hours for the EDX map acquisition in order to try and avoid significant sample drift.

An EDX map affected by sample drift is shown in Figure 6.86. The figure shows the SEM micrograph (a) of an intermetallic of interest together with an EDX map of silicon that has not been affected by sample drift (b) and an EDX map of the same region that has been affected by sample drift (c). The outline of the intermetallic in the x-ray map is clear and sharp in the drift free map while the entire outline of the intermetallic appears as a smudge in the drifted map. When the sample drifts the x-rays from the intermetallic are emitted from a new region in the map and as the map is built up of multiple scans this leads to increasing signal intensity in a region previous free of signal, blurring the original outline.

Figure 6.86 SEM micrograph of an intermetallic of interest (a). EDX map of silicon unaffected by sample drift (b) and an EDX map of the same region affected by sample drift (c).

6.6.2 Carbon contamination

Exposure of a beryllium test specimen to the corrosion solution for 15 minutes led to a dramatic increase in the intensity of the carbon Auger compared to the as-received intensity and the intensity of the carbon Auger observed during the aluminium corrosion investigation. The resultant spectrum appeared unusable because of the intense carbon Auger dominating the spectrum and the extremely short attenuation length of Be KLL Auger electrons. The carbon contamination was thought to have originated from a number of possible sources: out gassing of the glovebox, contaminated glassware and contaminated water in the corrosion solution or rinse water.
Outgassing of plastic is caused by the gradual leaching of minor components within a plastic into the environment. This was ruled out as the cause of the contamination after a UV-ozone cleaned sample was left exposed inside the glovebox for 12 hours prior to analysis. Analysis of the sample revealed only extremely low levels of carbon present on the surface of the sample, consistent with the sample being exposed to air for a short period. To test the DDI rinse water a UV-ozone cleaned sample of aluminium was rinsed with water for ten seconds and analysed. The spectrum showed a large carbon Auger transition. Following this the DDI washer was replaced with ultra pure water purchased from Sigma-Aldrich. Additionally, the glassware was replaced with freshly cleaned glassware that was given a final rinse in the ultra pure water. The aluminium was reanalysed after rinsing with this solution and a weak carbon Auger was observed.

Following elimination of carbon contamination resulting from the water used in the experiment, another beryllium test specimen was immersed into a fresh sodium chloride solution for 45 minutes and rinsed. The sample again showed an intense carbon Auger and so the problem was examined further. Two polished test specimens one of aluminium and one of beryllium were placed into the solution of sodium chloride in the same freshly cleaned beaker. The samples were left for 45 minutes before being removed. Their surfaces were rinsed with ultra pure water with the excess drained onto lint free tissue. The samples were then both placed into the spectrometer. Each were analysed from ten regions on the sample surface spread over a number of millimetres. The results from five of the points on beryllium and aluminium are shown in Figure 6.87 and Figure 6.88 respectively. The spectra in these figures illustrate that while the C KLL Auger transition is weak in the spectra collected from aluminium, it is considerably more intense in the spectra from beryllium.

The significant difference in the observed intensities for the two materials exposed to the same conditions led to the belief that the effect may be intrinsic to beryllium. XPS was carried out to further probe the contamination.

![Figure 6.87 AES survey spectra collected from five points spread across a beryllium sample which was exposed to the NaCl solution.](image-url)
The aluminium and the beryllium specimens were analysed, using the Theta Probe spectrometer, in three regions from across the surface with a 400 \( \mu \text{m} \) x-ray spot. Representative spectra from beryllium and aluminium are shown in Figure 6.89 and Figure 6.90 respectively. From these spectra the oxide thicknesses were calculated as 3.9 nm and 6.4 nm for beryllium and aluminium. The concentration of carbon on the surfaces of beryllium and aluminium were found to be fairly constant ~20 at.% and 25 at.% respectively, these correspond to contamination thicknesses of 0.44 nm and 0.58 nm respectively.
The XPS results help to solve the problem of the high intensity of the C $KLL$ on beryllium. Exposure to an aqueous solution does not lead to more carbon contamination depositing onto a beryllium surface compared to an aluminium surface. The presence of the sharp Be $KLL$ Auger transition indicates that the carbon contamination was not as thick as could be implied from the observed intensity of the carbon Auger in the spectrum. This is justified by the low escape depth of the 100 eV Be $KLL$ electrons which is ~1.5 nm. The relative intensity between the oxygen and the carbon Augers for the aluminium and beryllium samples cannot be used as a gauge for the thickness of carbon as the oxide layer was so much thicker on the aluminium specimen and the O $KLL$ transition would be more intense. The Al $KLL$ is present in the spectrum at 1400 eV kinetic energy. However, the Be $KLL$ is present at 100 eV. These transitions are generated from very different depths within the sample and are effected to different extents by a carbon over layer. As such the intensity of the Al $KLL$ is affected less by the over layer.

Despite obtaining newly purchased glassware which was rinsed using ultra-pure water and then heated in an oven to 250 °C for 10 hours and placing the sample in a petri dish to maximise the size and minimise the thickness of any carbon contamination forming meniscus. Significant carbon contamination was still observed on the surface following long submersion times.

This evidence suggests that the large concentration of carbon present at the surface is intrinsic to beryllium and the effect of attenuation of the metal surface electrons must be accepted as part of the experimental work. This effect has been observed in the past in the surface analysis laboratory. Copper surfaces are known or remaining fairly clean while steel surfaces require incredibly clean conditions to remain free of significant carbon contamination.

6.7 Conclusions
Different corrosion processes were observed depending upon the composition of the second phase particles.
Elemental silicon inclusions were not found to initiate pitting corrosion. No signs of activity were associated with Intermetallic #6, a large single phase silicon inclusion. Additionally, the presence of an AlFeBe₄ precipitate, in the case of Intermetallic #5, did not appear to effect the benign nature of the inclusion.

The large alumina second phase particles all appeared to be present in the metal with a crack at the matrix/particle interface. This was found to act as a site for crevice corrosion with the anodic dissolution of subsurface matrix adjacent to the particle and the deposition of beryllium hydroxide at the crevice mouth. The severity of crevice corrosion varied with the inclusion. While Intermetallic #8 showed the apparent formation and subsequent passivation of a pit, Intermetallic #9 showed active crevice corrosion throughout the immersion time.

The complex composition of Intermetallic #4 was believed to result of mixed, particularly hydrolysed, beryllium carbide with aluminium oxide. The particle demonstrated initial anodic behaviour before switching to a crevice corrosion process as was observed for alumina particles.

The activity of the AlFeBe₄ precipitates appeared not to be linked to their morphology or geometry but to the presence of damage at the surface of the inclusion, as in the case of Intermetallic #1. This damage likely disrupted the passive film and provided sites for the stagnation of electrolyte and the onset of an oxygen differential cell to initiate corrosion. The deposition of corrosion products led to the formation of a dome over the particle and adjacent matrix which hindered diffusion and slowed the corrosion process.

The behaviour of Intermetallic #7 the Ti₃Si type intermetallic was similar to the active AlFeBe₄ precipitate with the formation of an initial ring of corrosion products a constant distance from the centre of the particle. This ring developed into a dome that appeared to prevent further corrosion.

The intermetallic types AlFeBe₄ and Ti₃Si both appeared to be anodic in to the surrounding matrix. The bulk of the particles appeared to remain with the preferential dealloying of beryllium. Fine copper particles were observed to deposit onto these anodic regions.

It is believed that dealloying together with the deposition of copper would lead to the eventual reverse in galvanic activity such that the particle becomes cathodic with the matrix.

In the next chapter the effect of vapour degreasing beryllium samples using chlorinated solvents will be explored. Chlorides formed at a metal surface during degreasing are believed to act as corrosion precursors upon exposure to moisture in the environment. In an effort to address the compatibility of a wider range of solvents than those previously tested experimentally, six solvents with different molecular constraints were studied.
Chapter 7 - The Effect of Chlorinated Solvents on Beryllium

7.1 Introduction

Prior to use or long term storage, finished metal components will often undergo a vapour degreasing stage to remove various soils including finger prints, lubricating oil and machining coolants [113]. It is known that the cleaning of reactive metals, such as aluminium, with chlorinated solvents requires the addition of inhibitors or stabilisers to prevent the formation of metal chlorides [114,115]. If these inhibitors are not added the reaction between the metal and the solvent can become self catalytic, consuming the solvent in a highly energetic, exothermic, reaction that can evolve phosgene gas which can have fatal consequences for the equipment operator [116].

Although a wide range of solvents have been investigated for use with aluminium and other technologically important alloys, beryllium has received little experimental attention. It is expected that the behaviour of beryllium when exposed to these solvents will be similar to other reactive metals coated with a passivating oxide, such as aluminium, resulting in the formation of beryllium chloride at the metal surface. The metal chloride is regarded as a corrosion precursor because when the alloy is exposed to a humid environment the chloride reacts with water to form insoluble metal hydroxide and hydrochloric acid. This reaction is shown in Equation 7.1 for beryllium. The beryllium chloride is highly soluble in water. With a solubility of ~5.3 mol dm$^{-3}$ at room temperature [37]. The presence of chloride ions in solution, from the hydrochloric acid that is produced from the reaction, results in accelerated corrosion of beryllium [7].

$$\text{BeCl}_2 + 2\text{H}_2\text{O} \rightarrow \text{Be(OH)}_2 + 2\text{HCl} \quad \Delta H = -142 \text{ kJ mol}^{-1} \quad (7.1)$$

From the literature discussed in Chapter 2, only one report was located which related to the experimental testing of chlorinated cleaning solvents on beryllium. These solvents were: trichloroethane (TCA), trichloroethene (TCE) and carbon tetrachloride (CCl$_4$) [36]. Also briefly mentioned in Chapter 2 was a thermodynamic study that modelled seventeen solvents, each containing 1, 2 or 6 carbon atoms per molecule [5,35]. The results of the study suggested two requirements for beryllium chloride formation, these being: that carbon is essential to form beryllium chloride from beryllium oxide and the H:Cl ratio in the solvent molecule must be less than 1. These results were not verified experimentally within the investigation.

The thermodynamic modelling used a commercially available program called Thermo-Calc. This program is thermodynamic calculation software package designed for dealing with complex systems with many interdependent reactions. It relies on databases of the Gibbs free energy and reaction equilibriums to collate information for the model. An example of a phase diagram produced by the model for beryllium corrosion is shown in Figure 7.1. The system components that the model used to generate the diagram consisted of beryllium, carbon, oxygen, hydrogen and the solvent molecules at room temperature and pressure. The software combines the basic enthalpies of reaction for all of the possible reactions that can occur between the
constituents. It then produces the diagram to reflect which products are most likely to form based upon the different mole fractions of the reactants. The x axis is the molar ratio of carbon (in the solvent molecule) to oxygen (in the atmosphere) and the y axis is the molar ratio of hydrogen to chlorine (in the solvent molecule). As is the case for metallographic phase diagrams, passing over any of the lines results in one of the phases becoming unstable and unlikely to form, for example passing over the f-g line graphite is unstable. Each point of the diagram represents different atmospheric conditions and or different solvents being used to clean the surface. The phase diagram is useful in determining the best solvents for use in vapour degreasing of beryllium components.

Figure 7.1 Phase diagram to describe the material present on a beryllium metal surface with different hydrogen and carbon content. N is the number of moles of a constituent.

The diagram can be used to consider a solvent with a H:Cl greater than 1, such as 1,1,2-Trichloroethane (TCA), the diagram predicts that for these conditions that beryllium chloride does not form. From the diagram the stable phases under these conditions are BeO + H₂O and then BeO + C at higher oxygen concentrations. If a solvent is selected with a H:Cl of zero, such as CCl₄, the diagram predicts that beryllium chloride is only thermodynamically stable when the C:O₂ is greater than 1. This indicates that chloride formation was less likely for solvents with a low number of carbon atoms. If a solvent is selected with a H:Cl of <1, the diagram predicts that beryllium chloride is stable when the C:O₂ is greater than 1. As such solvents with a lower number of carbon atoms are again favourable to avoid chloride formation.

7.2 Experimental

7.2.1 Vapour degreasing

To test the conclusions of the previously described thermodynamic modelling and broaden the range of solvents experimentally tested for compatibility with beryllium, six solvents were selected from the seventeen that were modelled that did not include those previously studied. These are shown in Table 7.1 together with the additives they are known to contain. Three of the solvents could not be purchased without various additives. They represent a pair of solvents from each group of carbon atom content, i.e. containing 1, 2 or 6 carbon atoms in the solvent molecule. On the basis of the modelling one of each pair is expected to
form beryllium chloride from beryllium oxide while the other is not. The table shows the solvents in addition to information believed to be important based upon the conclusions from the thermodynamic study. The highest purity solvents that are still used for general cleaning purposes and that were readily available, were purchased.

Table 7.1 Solvents used in this investigation together with their known additives and the predicted formation of BeCl₂ based upon thermodynamic calculations. *Mono methyl ether hydroquinone

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Predicted BeCl₂</th>
<th>H:Cl in solvent</th>
<th>C in solvent</th>
<th>Concentration</th>
<th>Known additives</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>Yes</td>
<td>1:3</td>
<td>1</td>
<td>&gt;99.0%</td>
<td>0.5-1.0% ethanol as stabiliser</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>No</td>
<td>2:2</td>
<td>1</td>
<td>&gt;99.5%</td>
<td>50 ppm amylene as stabiliser</td>
</tr>
<tr>
<td>Tetrachloroethene</td>
<td>Yes</td>
<td>0:4</td>
<td>2</td>
<td>&gt;99.0%</td>
<td>-</td>
</tr>
<tr>
<td>1,1-Dichloroethene</td>
<td>No</td>
<td>2:2</td>
<td>2</td>
<td>&gt;99.0%</td>
<td>200 ppm MEHQ* as inhibitor</td>
</tr>
<tr>
<td>Pentachlorobenzene</td>
<td>Yes</td>
<td>1:5</td>
<td>6</td>
<td>&gt;99.5%</td>
<td>-</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>No</td>
<td>5:2</td>
<td>6</td>
<td>&gt;98.0%</td>
<td>-</td>
</tr>
</tbody>
</table>

All of the solvents used in this work were purchased from Sigma-Aldrich and the polished beryllium samples were supplied by AWE. 1 cm² samples of beryllium S-65 were wet ground to a 1 μm finish. Subsequently they were ultrasonically cleaned and rinsed in DDI water. They were stored, wrapped in aluminium foil, in polypropylene bags with a silica gel desiccant prior to the investigation. Samples were UV-Ozone cleaned for ten minutes at a reduced pressure of 133 mbar using a Hitachi SEMZONE cleaner, immediately prior to the initial XPS analysis. Vapour degreasing was performed using the rig shown in Figure 7.2. A 250 ml round bottom flask was clamped into a retort stand and placed inside a heating mantle, 100 ml of the selected solvent was then added to the RBF. A reflux condenser was connected to the round bottom flask and lightly clamped. A beryllium sample was suspended at the bottom of the condenser tube using platinum wire. The temperature was slowly increased to the boiling point of the solvent. The height of the sample and the flow rate of cooling water were adjusted so that the solvent vapours condensed upon the sample. The degreasing was continued for twenty minutes, after which the solvent was allowed to cool to room temperature and the beryllium coupon was removed.
The specimens were mounted on stainless steel sample holders using a stainless steel screw. The solvent exposed samples were then analysed by XPS. After this analysis was completed the coupons where rinsed with copious amounts of DDI water and analysed again. Finally two samples were mechanically abraded while submerged in chloroform or dichloromethane and reanalysed. Between each analysis the samples were wrapped in aluminium foil and stored in a desiccator.

XPS was performed using a Thermo Scientific Theta Probe spectrometer, previously described in Chapter 3, and a VG Scientific ESCA Mk II spectrometer fitted with an Alpha 110 analyser, as shown in Figure 7.3. XPS spectra were acquired using monochromated Al Kα (400 μm spot) and achromatic Al Kα (6 mm spot) X-ray sources (hv = 1486.68 eV). All spectra were referenced to the C 1s peak at 285.0 eV. Pass energies of 300, 80 and 50 eV were used for the survey spectra and high resolution spectra respectively. Energy step sizes of 0.3 and 0.1 eV were used for survey spectra and high resolution spectra. The electron take off angle was 53° and 45° from the sample normal in the Theta Probe and ESCA Mk II respectively. The ESCA Mk II
was used for the majority of the experimental XPS, as it provided a larger analysis area than the Theta Probe and was available for use at all times over the course of this part of the work.

Peak fitting was carried out for the Cl 2p region, the peak FWHM was fixed to 2.1 eV. The Cl 2p\textsubscript{3/2}-2p\textsubscript{1/2} peak separation was set to 1.6 eV and the Cl 2p\textsubscript{3/2} to Cl 2p\textsubscript{1/2} peak height ratio was set to 2:1 and a 5% variance was allowed. The inorganic Cl 2p\textsubscript{3/2} component was set in binding energy to 198.2-198.5 eV and the organic Cl 2p\textsubscript{3/2} component was 200.2-200.5 eV. A Shirley background subtraction was used for calculating peak areas and Wagner sensitivity factors used for quantification [117].

The thickness of the carbon contamination layer at each stage of analysis was calculated using the atomic concentration fraction of carbon. Equation 7.2 gives an example of this method [118]:

$$d = -\lambda_{\text{carbon}} \cos \theta \ln(1 - c) \quad (7.2)$$

Where:

- $d$ is the thickness of the carbon overlayer,
- $\lambda_{\text{carbon}}$ is the attenuation length of C 1s electrons in carbon (3.3 nm),
- $\theta$ is the electron take off angle, and
- $c$ is the concentration of carbon.

Below is an example of the equation used to calculate the thickness of carbon present on a sample with 30 at.% carbon at the surface.

$$d = -3.3 \cos 45 \ln(1 - 0.7)$$

$$d = -2.3 \ln(0.3)$$

$$d = 0.82 \text{ nm}$$

The thickness of the oxide was calculated using the relative areas of the metal and oxide peaks [119]. Equation 7.3 gives an example of this method:

$$d = \lambda_{\text{ox}} \sin \theta \ln \left( \frac{(N_{\text{ox}} \lambda_{\text{ox}} I_{\text{ox}})}{(N_{\text{m}} \lambda_{\text{m}} I_{\text{m}})} + 1 \right) \quad (7.3)$$

Where:

- $\theta$ is the electron take off angle,
- $\lambda_{\text{ox}}$ and $\lambda_{\text{m}}$ are the inelastic mean free path of electrons in the oxide and metal respectively,
- $N_{\text{ox}}$ and $N_{\text{m}}$ are the volume densities of the metal atoms in the oxide and metal and $I_{\text{ox}}$ and $I_{\text{m}}$ are the relative areas of the oxide and metal peaks. The values required for the calculation are shown in Table 7.2.
Below is an example of the calculation for a beryllium sample, in the ESCA Mk II, for which the oxide and metal peak intensities were measured as 17,500 count s\(^{-1}\) and 11,700 counts s\(^{-1}\) respectively.

\[
d = 3.4 \sin 45 \ln \left( \frac{(1.69 \times 2.6 \times 17,500)}{(1 \times 3.4 \times 11,700)} + 1 \right)
\]

\[
d = 2.4 \ln \left( \frac{72,800}{39,780} + 1 \right)
\]

\[
d = 2.5 \text{ nm}
\]

Table 7.2 Values used in calculating the thickness of carbon contamination and the oxide layer present on aluminium and beryllium. *IMFP has been used in place of the attenuation length [120], aluminium values are included for the aluminium investigation.

<table>
<thead>
<tr>
<th>Term</th>
<th>Symbol</th>
<th>Value</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Take off angle</td>
<td>( \theta )</td>
<td>45</td>
<td>45</td>
<td>degrees</td>
</tr>
<tr>
<td>Volume density of metal</td>
<td>( N_m )</td>
<td>1.5</td>
<td>1.69</td>
<td>-</td>
</tr>
<tr>
<td>Volume density of oxide</td>
<td>( N_{ox} )</td>
<td>1.0</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>Attenuation length* in metal</td>
<td>( \lambda_m )</td>
<td>2.6</td>
<td>2.6</td>
<td>nm</td>
</tr>
<tr>
<td>Attenuation length* in oxide</td>
<td>( \lambda_{ox} )</td>
<td>2.8</td>
<td>3.4</td>
<td>nm</td>
</tr>
<tr>
<td>Attenuation length* in carbon</td>
<td>( L_c )</td>
<td>3.3</td>
<td>3.3</td>
<td>nm</td>
</tr>
</tbody>
</table>

### 7.2.2 Ozone cleaning

The use of UV-Ozone cleaning of the sample surfaces was investigated after discovering that the surface of one of the samples analysed during the investigation was heavily contaminated with hydrocarbon material following water rinsing. Ozone cleaning is normally utilised for the preparation of samples for electron microscopy because contamination on the sample can interfere with: ultra-high resolution imaging, low energy analysis as well as extended acquisition x-ray mapping.

In electron microscopy the thin layer of carbon contamination present on sample surface undergoes pyrolysis and forms a solid structure on the surface. This is known as “black box” in SEM. An example of this is shown in Figure 7.4. This build up of material leads to a significant decrease in the clarity of the electron image. Some of this carbon originates from the microscope vacuum but the majority of it is already present on the sample surface [97].

![Figure 7.4](image-url) SEM micrographs of beryllium that produced the black box effect. (a) a significant effect on a freshly polished surface (b) a very light black box following ozone cleaning.
A schematic of the processes involved in ozone cleaning is shown in Figure 7.5. A specimen is placed inside the vacuum chamber of the ozone cleaner and the chamber is evacuated to the chosen pressure. The gentlest cleaning is performed at high pressure and more aggressive cleaning at lower pressures. The greater the pressure the more likely the generated radical species are to react with material already in the gas phase and not the sample surface, so fewer reach the surface giving a gentler clean. For a metal sample the lowest operational pressure is used which is ~133 mbar. Once the appropriate pressure is obtained, a low-pressure mercury discharge lamp generates two wavelengths of UV radiation, 189 and 254 nm. The shorter wavelength is absorbed by oxygen which photodissociates into atomic oxygen. These radicals react with oxygen to form ozone.

![Figure 7.5 Schematic of the reactions occurring within the ozone cleaner on a contaminated sample surface.](image)

The longer wavelength photons are absorbed by ozone leading to dissociation back into oxygen and atomic oxygen. These photons can also react with the hydrocarbon contamination resulting in photolysis and breakdown. The atomic oxygen is a powerful oxidising agent and reacts with the hydrocarbon contamination to form gaseous species which are then pumped out of the chamber by the vacuum pump.

The two wavelengths of UV correspond to photon energies of 647 kJ mol\(^{-1}\) (6.7 eV) and 472 kJ mol\(^{-1}\) (4.9 eV). By examining various chemical bond energies common in hydrocarbon contamination, as shown in Table 7.3, it can be seen that the majority of organic bonds can be dissociated by the action of either one or both of the wavelengths of ultraviolet radiation.

Table 7.3 Bond energies for common organic chemical bonds

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Energy (kJ mol(^{-1}))</th>
<th>Bond</th>
<th>Bond Energy (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-O</td>
<td>139</td>
<td>C≡C</td>
<td>607</td>
</tr>
<tr>
<td>O=O</td>
<td>490</td>
<td>C=O</td>
<td>724</td>
</tr>
<tr>
<td>O-H</td>
<td>463</td>
<td>C-Cl</td>
<td>328</td>
</tr>
<tr>
<td>C-C</td>
<td>348</td>
<td>H-F</td>
<td>563</td>
</tr>
<tr>
<td>C-H</td>
<td>413</td>
<td>C-F</td>
<td>441</td>
</tr>
<tr>
<td>C-N</td>
<td>292</td>
<td>H-Cl</td>
<td>432</td>
</tr>
<tr>
<td>C-O</td>
<td>352</td>
<td>N-H</td>
<td>310</td>
</tr>
</tbody>
</table>
Chapter 7

Chlorinated Solvents

7.3 Aluminium alloy test specimen

7.3.1 Introduction

As described in Chapter 6, the safety of the researcher and laboratory staff was paramount in this project. Prior to the use of beryllium, a full run through of the experiment was completed using a non-toxic aluminium analogue. The sample used for this test run was a coupon of AA2219 which was available from a previous project. The sample was wet ground and polished to a 1 µm finish.

7.3.2 Surface analysis using XPS

7.3.2.1 Initial surface

After polishing and rinsing the AA2219 sample in acetone and DDI water the specimen was analysed by XPS. Figure 7.6 shows the survey spectrum that was collected, using the ESCALAB Mk II, from the as-polished alloy. The most intense peaks are the O 1s, C 1s and Al 2p and Al 2s. A weak Cu 2p peak was also observed from the copper present in the alloy. Contamination elements are also present. These include silicon, calcium and fluorine.

![Figure 7.6 Survey spectrum from the AA2219 sample surface.](image)

A moderately thin carbon over layer is present, this can be inferred by the positive, rising background to the higher binding energy side of the aluminium peaks, whilst the background after the C 1s peak is negative. The carbon concentration was calculated as 30 at.%. From this the thickness of carbon contamination was calculated as 0.9 nm. Additionally the thickness of aluminium oxide was calculated as 3.6 nm. The Cl 2p region was collected but showed no detectable chlorine.

7.3.2.2 Chloroform treated surface

Following vapour degreasing using chloroform, some small changes were observed in the survey spectrum, as shown in Figure 7.7. A small Cl 2p peak was apparent at ~200 eV and the silicon and fluorine peaks were no longer observed. Indicating they were surface contaminants. The concentration of carbon was found to be 33 at.% and from this the thickness of contamination was calculated as 1.0 nm. Additionally, the oxide layer thickness was calculated as 3.6 nm. The thickness of carbon contamination was essentially unchanged from the as-cleaned surface. However, as the thickness of carbon contamination was already very low, a large change was not expected.
A high resolution spectrum of the Cl 2p peak that was observed in the survey spectrum was acquired and peak fitting of the envelope was performed, this peak is shown in Figure 7.8. The peak fitting parameters previously described in the experimental were used. The Cl 2p peak showed the presence of inorganic and organic forms of chlorine. This showed that chlorine from the solvent had reacted with the base aluminium metal to form aluminium chloride, at the sample surface. Quantification of the high resolution spectra revealed the presence of 0.32 at.% organic chlorine and 0.43 at.% inorganic chloride.

**7.3.2.3 Rinsed surface**

As part of the assessment of the vapour degreasing it was desired to ascertain if the metal chloride that formed on the surface could be removed by rinsing the surface with DDI water. To examine this possibility, the aluminium specimen was thoroughly rinsed in the laboratory DDI water and then analysed again by XPS. The survey spectrum collected after rinsing is shown in Figure 7.9. Examination of the spectrum showed steep positive backgrounds are present to the higher binding energy side of the O 1s, O KLL, Al 2s and Al 2p peaks. The large increase in the intensity of the C 1s and C KLL together with the negative background following these peaks showed that the level of carbon contamination at the surface was significantly higher than the as-polished or the vapour degreased sample surface.
Figure 7.9 Survey spectrum from the aluminium surface after exposure to chloroform and then rinsed with DDI water. The large increase in hydrocarbon contamination showed that the water source in the laboratory was poor. Upon further investigation the filters in the purifier had exceeded their lifetime resulting in significant impurities in the water. The concentration of carbon contamination was found to be 87 at.%. From this the thickness of the contamination was calculated as 5.2 nm. The thickness of the aluminium oxide was calculated as 3.61 nm. Indicating no change in the oxide thickness.

A high resolution Cl 2p spectrum was collected and showed no detectable level of chlorine. However, because of the extremely high level of carbon present at the surface it was not representative of the true state of the surface as the electrons from the surface would be highly attenuated by the thick carbon over layer, significantly reducing the intensity of the photoelectron peaks of interest. It was decided to repeat the investigation after cleaning the aluminium surface, to enable accurate conclusions to be drawn.

The aluminium sample that produced the spectrum shown in Figure 7.9 was UV-Ozone cleaned for 10 minutes at 133 mbar and then analysed by XPS. The survey spectrum is shown in Figure 7.10. The striking reduction in the intensity of the C 1s and the increase in intensity of the aluminium and oxygen peaks are immediately apparent. The carbon concentration was found to be 21 at.% resulting in a calculated value of 0.6 nm for the thickness of the contamination layer. The reduction in thickness shows the effectiveness of UV-Ozone cleaning to remove hydrocarbon contamination. The thickness of aluminium oxide was calculated as 4.30 nm. An increase of 0.7 nm compared to the degreased, water rinsed sample surfaces and the native air formed oxide thickness, indicating a degree of oxidation to even the highly insulating oxide layer on aluminium. Vapour degreasing was not repeated on the aluminium sample after this point to focus on the beryllium samples.
7.3 Vapour degreased beryllium samples

7.3.1 Introduction
Following the establishment of a safe protocol for the experiment using aluminium the analysis of beryllium was undertaken. A number of additional safety precautions were added to the experimental procedure to minimise the risk of the uncontrolled release of beryllium. These included: disposal of all chlorinated solvent waste into non-communal chlorinated solvent Winchesters. These were marked as hazardous and that they possibly contained beryllium. Additionally, the water from the rinsing step was also added to non-communal aqueous waste Winchesters that were labelled as containing beryllium. Finally, all of the blotting tissue and gloves used in the handling of the beryllium pieces were disposed of as hazardous waste.

7.3.2 Initial surface
Each sample of beryllium was UV-Ozone cleaned for 10 minutes prior to analysis to remove as much carbonaceous contamination as possible and ensure that all samples had a near uniform level of hydrocarbon contamination at the surface. Figure 7.11 shows a typical survey spectrum collected from the beryllium samples after ozone cleaning. In each case quantification of all the elements was performed. Additionally, the oxide layer thickness and thickness of the hydrocarbon contamination layer was calculated. Table 7.4 shows the calculated values for oxide and contamination layer thicknesses. Each sample in the table was named according to the solvent that it was ultimately exposed to.

A number of samples showed the presence of a small sodium peak indicating traces of sodium chloride contamination. It was believed this contamination may have originated from the water used to polish the samples. To remove the salt, the samples were rinsed in hot DDI water before UV-ozone cleaning. Following the additional rinse, the surfaces all appeared free of sodium. Figure 7.12 shows the high resolution Cl 2p spectra from the six samples following cleaning. They show that no detectable concentration of chlorine is present on the surfaces of the beryllium samples prior to the vapour degreasing experimental stage.
Figure 7.11 A typical survey spectrum from an ozone cleaned beryllium sample.

Table 7.4 Calculated oxide and contamination layer thicknesses from all of the beryllium samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oxide thickness (nm)</th>
<th>Contamination thickness (nm)</th>
<th>Carbon concentration (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>2.62</td>
<td>0.65</td>
<td>24.4</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>2.75</td>
<td>0.33</td>
<td>13.1</td>
</tr>
<tr>
<td>Tetrachloroethene</td>
<td>2.67</td>
<td>0.34</td>
<td>13.5</td>
</tr>
<tr>
<td>1,1-Dichloroethene</td>
<td>2.68</td>
<td>0.39</td>
<td>15.3</td>
</tr>
<tr>
<td>Pentachlorobenzene</td>
<td>2.54</td>
<td>0.42</td>
<td>16.3</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>2.53</td>
<td>0.51</td>
<td>19.6</td>
</tr>
</tbody>
</table>

Figure 7.12 High resolution Cl 2p spectra from the six samples after rinsing in hot DDI water and UV-Ozone cleaning.

7.3.3 Vapour degreased samples

7.3.3.1 Analysis of solvent exposed surfaces

Each beryllium sample was vapour degreased for twenty minutes before being removed from the solvent vapours. After the sample had dried and cooled it was transferred to the spectrometer for analysis. Figure 7.13 shows a typical survey spectrum from a beryllium sample exposed to the chloroform vapours. The most apparent difference between this spectrum and that shown in Figure 7.11, is the appearance of the Cl 2p and Cl 2s photoelectron peaks at ~200 eV and 269 eV respectively. The Cl 2s peak is separated from the C 1s Kα,3,4 peak by about 6 eV and so the C 1s Kα,3,4 label has been omitted from the figure. In addition to the photoelectron peaks, a strong Cl LMM Auger transition is observed at ~1303 eV. This overlaps with the Mg 1s peak but it is possible to establish that no magnesium was present on the sample surface as magnesium
has strong KLL Auger transitions at ~305 eV and 310 eV and these were not observed in any of the survey spectra collected from the samples. Table 7.4 shows the calculated values for oxide and contamination thicknesses following solvent treatment.

![Image](https://via.placeholder.com/150)

**Figure 7.13 A typical survey spectrum from a chloroform vapour degreased beryllium sample.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oxide thickness (nm)</th>
<th>Contamination thickness (nm)</th>
<th>Carbon concentration (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>2.62</td>
<td>0.43</td>
<td>17.0</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>2.60</td>
<td>0.40</td>
<td>15.8</td>
</tr>
<tr>
<td>Tetrachloroethene</td>
<td>2.73</td>
<td>0.33</td>
<td>13.1</td>
</tr>
<tr>
<td>1,1-Dichloroethene</td>
<td>2.70</td>
<td>0.56</td>
<td>21.2</td>
</tr>
<tr>
<td>Pentachlorobenzene</td>
<td>3.73</td>
<td>0.79</td>
<td>28.8</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>2.68</td>
<td>0.68</td>
<td>25.4</td>
</tr>
</tbody>
</table>

High resolution Cl 2p spectra were collected from each of the samples following degreasing and the peak envelope fitted, according to the details in the experimental section, with organic and inorganic components. Table 7.13 shows the high resolution spectra from each of the samples following peak fitting. Five of the solvents show moderately intense inorganic Cl 2p3/2 and Cl 2p1/2 peaks at 198.2 eV and 199.8 eV respectively in addition to much weaker organic Cl 2p3/2 and Cl 2p1/2 peaks at 200.3 eV and 201.9 eV respectively. One of the solvents, pentachlorobenzene, shows considerably more intense organic chlorine peaks compared to the inorganic chlorine peaks. This is further discussed in the next section, but it is clear that the high level of retained solvent accounts for at least some of the apparent increase in the hydrocarbon contamination, particularly for the pentachlorobenzene exposed sample.
Figure 7.14 High resolution Cl 2p spectra from each of the analysed samples. (a) chloroform, (b) dichloromethane, (c) tetrachloroethene, (d) dichloroethene, (e) pentachlorobenzene and (f) chlorobenzene.

Quantification was performed from the high resolution spectra from all of the elements collected from each of six sample surfaces. Table 7.6 shows the quantification for the concentrations of inorganic and organic chlorine on each of the samples.

Table 7.6 Chlorine concentrations as found on the surfaces of each of the six samples

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Predicted BeCl₂</th>
<th>H:Cl in solvent</th>
<th>C in solvent</th>
<th>At.% Inorg Cl</th>
<th>At.% org Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>Yes</td>
<td>1:3</td>
<td>1</td>
<td>1.46</td>
<td>0.29</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>No</td>
<td>2:2</td>
<td>1</td>
<td>0.34</td>
<td>0.05</td>
</tr>
<tr>
<td>Tetrachloroethene</td>
<td>Yes</td>
<td>0:4</td>
<td>2</td>
<td>0.88</td>
<td>0.10</td>
</tr>
<tr>
<td>1,1-Dichloroethene</td>
<td>No</td>
<td>2:2</td>
<td>2</td>
<td>0.50</td>
<td>0.20</td>
</tr>
<tr>
<td>Pentachlorobenzene</td>
<td>Yes</td>
<td>1:5</td>
<td>6</td>
<td>0.57</td>
<td>4.56</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>No</td>
<td>5:2</td>
<td>6</td>
<td>0.83</td>
<td>0.09</td>
</tr>
</tbody>
</table>
7.3.3.2 A problem with pentachlorobenzene

Pentachlorobenzene was the only solvent tested that was not liquid at room temperature. Following degreasing the sample was immediately removed from the hot condenser tube. Unfortunately, upon cooling, it was observed that a thin film had formed on the sample surface. Figure 7.15 shows RLM images of the sample surface following degreasing, (a) shows the general appearance of the film at low magnification and (b) shows the individual condensed and solidified droplets of pentachlorobenzene. The presence of the film explains why the concentration of organic chlorine was so much higher on the pentachlorobenzene sample compared to the samples vapour degreased using the other five solvents. All of the other sample surfaces appeared the same as the as polished surface when examined by RLM.

![Figure 7.15 RLM images of the beryllium sample vapour degreased using pentachlorobenzene, (a) low magnification, (b) higher magnification.](image)

7.3.4 Rinsed samples

Following the analysis of all the samples after vapour degreasing, each sample was removed from the spectrometer and rinsed for one minute with DDI water and gently brushed using a wet laboratory grade Kimwipe. Each of the samples was then reanalysed. Figure 7.16 shows a typical survey spectrum, from the sample exposed to chloroform, following rinsing. The survey spectra appeared almost identical to those collected from the original sample surfaces, except for a slight increase in the intensity of the C 1s peak. The Cl 2p and the Cl LMM Auger transition were no longer observed. Table 7.7 shows the calculated values for oxide and contamination thicknesses.

![Figure 7.16](image)
Figure 7.16 Typical survey spectrum collected from a beryllium sample surface, previously exposed to chloroform vapours, following rinsing.

Table 7.7 Calculated oxide and contamination layer thicknesses from all of the beryllium samples after degreasing and rinsing with water

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oxide thickness (nm)</th>
<th>Contamination thickness (nm)</th>
<th>Carbon concentration (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>2.53</td>
<td>0.65</td>
<td>24.4</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>2.73</td>
<td>0.67</td>
<td>25.0</td>
</tr>
<tr>
<td>Tetrachloroethene</td>
<td>2.58</td>
<td>0.86</td>
<td>30.9</td>
</tr>
<tr>
<td>1,1-Dichloroethene</td>
<td>2.50</td>
<td>0.58</td>
<td>21.9</td>
</tr>
<tr>
<td>Pentachlorobenzene</td>
<td>3.74</td>
<td>1.07</td>
<td>36.9</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>2.80</td>
<td>0.71</td>
<td>26.1</td>
</tr>
</tbody>
</table>

High resolution Cl 2p spectra were collected from each of the samples. The high resolution spectra from five of the solvents are shown in Figure 7.17 and the spectrum from pentachlorobenzene is shown in Figure 7.18. They show that for dichloromethane and 1,1-dichloroethene the inorganic and organic chlorine was completely removed by rinsing the sample surface. The samples exposed to chloroform and chlorobenzene still showed low concentrations of inorganic and organic chlorine, while the sample exposed to tetrachloroethene still showed a trace of inorganic chloride. The peak at the edge of the spectrum at ~191 eV is believed to be the P 2p peak, from phosphorus associated with the nickel impurity at the surface.

The high resolution spectrum from the sample exposed to pentachlorobenzene shows a reduction in the intensity of the organic chlorine peaks. Quantification from the fitted spectra is shown in Table 7.8. Trace levels of chlorine are present on three of the samples. However, the pentachlorobenzene sample has a significant amount of organic chlorine remaining on the surface. Optical examination of the surface revealed that the thin film of solidified solvent droplets remained on the surface.
Chapter 7

Chlorinated Solvents

Christopher F. Mallinson

Figure 7.17 High resolution Cl 2p spectra from five of the sample surfaces following rinsing.

Figure 7.18 High resolution Cl 2p spectrum from the sample vapour degreased using pentachlorobenzene and then rinsed.

Table 7.8 Chlorine quantification from the rinsed sample surfaces. *ND: not detected

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Predicted BeCl₂</th>
<th>H:Cl in solvent</th>
<th>C in solvent</th>
<th>At.% Inorg Cl</th>
<th>At.% org Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>Yes</td>
<td>1:3</td>
<td>1</td>
<td>0.11</td>
<td>0.09</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>No</td>
<td>2:2</td>
<td>1</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td>Yes</td>
<td>0:4</td>
<td>2</td>
<td>0.07</td>
<td>ND</td>
</tr>
<tr>
<td>1,1-Dichloroethene</td>
<td>No</td>
<td>2:2</td>
<td>2</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Pentachlorobenzene</td>
<td>Yes</td>
<td>1:5</td>
<td>6</td>
<td>0.23</td>
<td>2.04</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>No</td>
<td>5:2</td>
<td>6</td>
<td>&lt;0.06</td>
<td>&lt;0.04</td>
</tr>
</tbody>
</table>

7.4 Samples scribed under solvent

7.4.1 XPS of damaged region

Following analysis of all the samples following vapour degreasing and rinsing two further samples were analysed. One sample was submerged in chloroform and the other in dichloromethane at room temperature. These two solvents were selected as they produced the greatest and least amounts of inorganic chloride respectively. The surface of each submerged sample was mechanically abraded using a steel scribe to
remove the protective oxide film. Each of the samples were removed from the solvent and allowed to dry before being placed in the Theta Probe spectrometer. Each of the damaged regions were analysed using a 200 μm x-ray spot to isolate the spot on a region that was fully damaged. Figure 7.19 shows the RLM image of the damaged region from which the XPS analysis was performed on the sample submerged in chloroform.

![Figure 7.19 RLM image of the mechanically abraded surface of the sample submerged in chloroform.](image)

Survey spectra and high resolution spectra were collected from the scribed regions on both samples. The survey spectra from each are shown in Figure 7.20. In each case the intensity of all the photoelectron peaks appear similar. The only clear difference between the two spectra is the intensity of the Cl 2p peak which is noticeably more intense for the chloroform sample. The iron observed in the spectrum likely originated from the steel scribe. The high resolution Cl 2p spectra from both samples are shown in Figure 7.21. They show that the chlorine peak envelope is fully attributed to the inorganic chloride peak components and no organic contribution is observed. The intensity of the chloroform sample Cl 2p peak is almost double that of the Cl 2p peak from the dichloromethane sample. Quantification was performed on both samples and the concentrations of chloride were found to be for 2.89 at.% for the chloroform sample and 0.97 at.% for the dichloromethane sample. The oxide thickness for the chloroform sample was calculated as 4.42 nm and 4.57 nm for the dichloromethane sample and the thickness of carbon contamination of both samples was found to be 0.57 nm.

![Figure 7.20 Survey spectra from a beryllium sample mechanically abraded under dichloromethane and chloroform.](image)
Regions from off of the mechanically abraded region were also analysed. On both the chloroform and dichloromethane surfaces the concentration of chlorine in the undamaged region was found to be $<0.1$ at.%, considerably less than the surfaces of samples exposed to the solvent vapours. Figure 7.22 shows the high resolution Cl 2p spectra from these regions. They show how weak the chlorine peak is in comparison to the damaged regions shown in Figure 7.21.

**Figure 7.22** High resolution Cl 2p spectra from undamaged regions of the mechanically abraded samples.

### 7.4.2 Auger analysis of damaged region

In addition to the XPS analysis of the mechanically abraded regions of the surface, AES was also performed. This was carried out to ensure that the region analysed was completely confined to the damaged region. Figure 7.23 shows the SEM micrographs collected from the surface of the (a) damaged region and (b) an undamaged region. The areas marked with boxes show the regions over which the electron beam was rastered for collecting the Auger spectra.
Survey spectra and high resolution spectra of the Cl LMM Auger transition were acquired from each of the regions shown in the micrographs. The survey spectra are shown in Figure 7.23. These show intense Be KLL, C KLL and O KLL Auger transitions, consistent with the XPS results which showed a carbon contamination layer and an oxide film. The intensities of the Auger transitions are similar in the spectra collected from both the damaged and undamaged regions indicating the oxide thickness and carbon contamination layer thicknesses are about equal. A sharp Cl LMM Auger transitions is observed in the spectrum from the damaged region and not in the spectrum from the undamaged region, indicating that chloride formation is generally limited to the damaged surface.

This is highlighted by examining the high resolution Cl LMM spectra of the two regions. The damaged region shows an intense Cl LMM peak while the undamaged region shows no chlorine peak. A retard ratio of 2 was used and 50 scans were acquired for each of the high resolution spectra, as such, if chlorine is present on the undamaged surface it is likely below the detection limit for AES, ~0.1 at.%. 

Figure 7.23 SEM micrographs showing an Auger analysis region on a beryllium surface (a) mechanically damaged region and (b) undamaged region.

Figure 7.24 AES survey spectra from the damaged and undamaged surface regions of beryllium.
7.5 Long term exposure to chloroform

In addition to the previous short term vapour degreasing of samples, one sample was immersed in chloroform for 30 days, at room temperature, to investigate the effect of long term solvent exposure. The sample was UV-Ozone cleaned and XPS was performed on the sample prior to immersion. No chlorine was observed on the initial sample surface. The high resolution Cl 2p spectrum from the sample after 30 days is shown in Figure 7.26. Quantification showed there to be 0.3 at.% chloride and 0.15 at.% organic chlorine present at the surface. The thickness of the oxide before and after submersion was calculated as 2.62 nm and 2.54 nm respectively. The thickness of the carbon contamination was found to be 0.87 nm and 0.77 nm before and after immersion respectively.

7.6 Commercial cleaning solvents

7.6.1 Expanded investigation

In addition to investigating the chlorinated solvents, two commercially produced cleaning solutions from 3M™, were investigated as comparisons to the chlorinated solvents. These solvents are designed as “drop-in” replacements for dichloromethane in degreasing procedures. The solvents were HFE 71-DE and HFE 72-DE. Their compositions are shown in Table 7.9. These solvents incorporate nonfluorobutyl methyl ether in addition to Trans-1,2-dichloroethene. They are designed to provide a range of suitable cleaning solvent properties including: non-flammable, azeotropic, low toxicity and non-ozone depleting. The experimental
However, as the commercial solvents contained fluorine in addition to chlorine, the F 1s region was also recorded during analysis. The intensity of the F KLL was too weak to obtain a peak position from.

Table 7.9 Compositions of the two 3M\textsuperscript{TM} solvents

<table>
<thead>
<tr>
<th>Solvent additive</th>
<th>HFE 71-DE</th>
<th>HFE 72-DE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt.%</td>
<td>Wt.%</td>
<td></td>
</tr>
<tr>
<td>Methyl nonafluorobutyl ether (C\textsubscript{4}F\textsubscript{9}OCH\textsubscript{3})</td>
<td>50</td>
<td>10</td>
</tr>
<tr>
<td>Ethyl nonafluorobutyl ether (C\textsubscript{4}F\textsubscript{9}OC\textsubscript{2}H\textsubscript{5})</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>Trans-1,2-dichloroethene (t-DCE)</td>
<td>50</td>
<td>70</td>
</tr>
</tbody>
</table>

7.6.2 Initial surface

As with the previous solvent samples each sample was UV-Ozone cleaned for 10 minutes prior to analysis of the initial surface. Beryllium is produced via the reduction of beryllium fluoride and so finished beryllium metal contains trace concentrations of beryllium fluoride. Therefore even on the initial sample surface a trace of fluorine was detected. A shortage of polished beryllium coupons required that the samples that had previously been exposed to the chlorinated solvents be reused. The sample exposed to HFE 71-DE had previously been exposed to 1,1-dichloroethene and the HFE 72-DE sample was previously exposed to chlorobenzene. Both of the samples had been thoroughly rinsed in hot DDI water prior and had been ozone cleaned prior to the initial analysis.

High resolution Cl 2p and F 1s spectra were collected from the initial sample surfaces. These are shown in Figure 7.27. The spectra showed the presence of traces of organic chlorine and inorganic fluorine. The signal to noise in the spectra was particularly poor, indicating an extremely low concentration of chlorine and fluorine. Quantification, shown in Table 7.10, showed this to be the case. The sample exposed to HFE 71-DE showed \(-0.1\) at.% chlorine and \(-0.2\) at.% fluorine. The sample exposed to HFE 72-DE showed similar concentrations of chlorine and fluorine, being \(-0.05\) at.% and \(-0.2\) at.% respectively.

![Figure 7.27](image)

Figure 7.27 High resolution Cl 2p (a) and F 1s (b) spectra collected from two beryllium samples, prior to exposure to the commercial cleaning solutions.

Table 7.10 Chlorine and fluorine concentrations from the samples prior to exposure to the two commercial solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Predicted BeCl\textsubscript{2}</th>
<th>H:Cl in solvent</th>
<th>C in solvent</th>
<th>At.% Cl</th>
<th>At.% F</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFE 71-DE</td>
<td>No</td>
<td>2:2</td>
<td>2</td>
<td>0.11</td>
<td>0.22</td>
</tr>
<tr>
<td>HFE 72-DE</td>
<td>No</td>
<td>2:2</td>
<td>2</td>
<td>0.06</td>
<td>0.17</td>
</tr>
</tbody>
</table>

The thickness of the oxide layer and the carbon contamination present on the surface was calculated for the initial surfaces. These are shown in Table 7.11. The oxide layer thickness was comparable to the values...
calculated for the previous set of samples prior to solvent exposure. The carbon concentration was also similar to the levels that were observed on the post UV-Ozone cleaned samples.

Table 7.11 Calculated oxide and contamination layer thicknesses from both samples prior to exposure to the commercial solvents

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oxide thickness (nm)</th>
<th>Contamination thickness (nm)</th>
<th>Carbon concentration (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFE 71-DE</td>
<td>2.85</td>
<td>0.29</td>
<td>11.7</td>
</tr>
<tr>
<td>HFE 72-DE</td>
<td>2.72</td>
<td>0.27</td>
<td>11.1</td>
</tr>
</tbody>
</table>

7.6.3 Degreased sample surface

The experimental setup for the commercial cleaning solutions was the same as for the chlorinated solvents. Each of the samples was exposed to the solvent vapours for 20 minutes prior to analysis. The boiling points of the solvents were 41 °C and 45 °C for HFE 71-DE and HFE 72-DE respectively. The high resolution Cl 2p and F 1s spectra are shown in Figure 7.28. The spectra show that the signal to noise has not improved compared to the spectra collected from the initial surface. The positions of the peaks also appear to have remained the same. Additionally, no obvious changes were observed in the survey spectra collected from both samples. Quantification of the Cl 2p and F 1s peaks, from each of the samples, is shown in Table 7.12. This shows that there was little difference in the measured concentrations of chlorine and fluorine, the slight changes <0.1 at.% could simply be down to the positions at which the backgrounds were subtracted, as the spectra are so noisy. The small change in the concentrations suggests no reaction between the solvent and the oxide layer.

![Figure 7.28 High resolution Cl 2p (a) and F 1s (b) spectra from two beryllium samples following exposure to the commercial cleaning solutions.](image)

Table 7.12 Chlorine and fluorine concentrations from the samples exposed to the two commercial solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Predicted BeCl₂</th>
<th>H:Cl in solvent</th>
<th>C in solvent</th>
<th>At.% Cl</th>
<th>At.% F</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFE 71-DE</td>
<td>No</td>
<td>2:2</td>
<td>2</td>
<td>0.15</td>
<td>0.26</td>
</tr>
<tr>
<td>HFE 72-DE</td>
<td>No</td>
<td>2:2</td>
<td>2</td>
<td>0.09</td>
<td>0.27</td>
</tr>
</tbody>
</table>

The thickness of the oxide layer and the carbon contamination present on the surface was calculated for the vapour degreased sample surfaces. These are shown in Table 7.13. The oxide layer thickness was for the sample exposed to HFE 71-DE appeared to decrease while the sample exposed to HFE 72-DE appeared to increase. The apparent changes in the oxide layer thickness are not explained by a significant change in the thickness of the carbon concentration as it has increased by ~1 at.%. The carbon concentrations are lower than any of the samples exposed to the chlorinated solvents.
Table 7.13 Calculated oxide and contamination layer thicknesses from both samples following exposure to the commercial solvents

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oxide thickness (nm)</th>
<th>Contamination thickness (nm)</th>
<th>Carbon concentration (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFE 71-DE</td>
<td>2.52</td>
<td>0.30</td>
<td>12.2</td>
</tr>
<tr>
<td>HFE 72-DE</td>
<td>2.93</td>
<td>0.34</td>
<td>13.7</td>
</tr>
</tbody>
</table>

7.6.4 Rinsed surface

After exposing the two samples to the commercial cleaning solutions the samples were rinsed with DDI water and analysed again by XPS. The high resolution Cl 2p and F 1s spectra are shown in Figure 7.29. As with the previous spectra there is little change in the signal to noise although a slight decrease in the signal intensity of the F 1s for the HFE 72-DE samples apparent. Quantification from the samples is shown in Table 7.14. Quantification showed a slight reduction in the concentration of fluorine on the surface of the sample exposed to HFE 72-DE. However, once again, the slight changes in concentration are likely to be because of the amount of noise in the spectra and so the accurate determination of a peak area is difficult.

![Figure 7.29 High resolution Cl 2p (a) and F 1s (b) spectra from two beryllium samples after rinsing the surface with DDI water.](image)

Table 7.14 Chlorine and fluorine concentrations from the samples rinsed in DDI water

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Predicted BeCl₂</th>
<th>H:Cl in solvent</th>
<th>C in solvent</th>
<th>At.% Cl</th>
<th>At.% F</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFE 71-DE</td>
<td>No</td>
<td>2:2</td>
<td>2</td>
<td>0.13</td>
<td>0.25</td>
</tr>
<tr>
<td>HFE 72-DE</td>
<td>No</td>
<td>2:2</td>
<td>2</td>
<td>0.09</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Following rinsing of the sample surfaces the oxide layer thickness and carbon contamination thickness were calculated. The oxide layer appeared to have increased by 0.35 nm on the sample exposed to HFE 71-DE and decreased by 0.24 nm on the sample exposed to HFE 72-DE. These values are in line with those calculated from the initial surface. However, the carbon concentration has increased noticeably, leading to an increase in the carbon thickness by ~0.4 nm and 0.3 nm for the samples exposed to HFE 71-DE and HFE 72-DE respectively.

Table 7.15 Calculated oxide and contamination layer thicknesses from both samples following rinsing

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oxide thickness (nm)</th>
<th>Contamination thickness (nm)</th>
<th>Carbon concentration (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFE 71-DE</td>
<td>2.87</td>
<td>0.68</td>
<td>25.4</td>
</tr>
<tr>
<td>HFE 72-DE</td>
<td>2.69</td>
<td>0.58</td>
<td>21.9</td>
</tr>
</tbody>
</table>
7.7 Corrosion investigation of samples exposed to chlorinated solvents

As an extension to the investigation into the corrosion of beryllium, it was decided to compare samples exposed to different solvents to observe if the surface chloride had any effect on the corrosion process in DDI water. Three samples were selected for this investigation. These were: a clean beryllium sample, a pentachlorobenzene sample and a chloroform sample. These represented surfaces with: no chlorine, organic chlorine and chloride respectively. Vapour degreasing was repeated for the pentachlorobenzene and chloroform samples. Each of the samples was imaged using RLM at a range of magnifications to assess the initial surface appearance. Following imaging, each of the samples was placed into a clean glass beaker filled with 30 ml of DDI water. Each beaker was lightly covered with aluminium foil to prevent airborne contamination. After 5, 10, 15, 30 days the samples were removed dried on tissue and their surfaces examined using RLM. The surface was examined for signs of pitting corrosion and if no pits or evidence of activity could be located, representative images of the surface were collected.

Gas bubbles were observed to accumulate on the sides of the sample exposed to chloroform when it was left to corrode. These were not observed on the other two samples. These may have been produced by the hydrolysis of carbides present at the surface of beryllium. Discussed in Chapter 2 were the two reactions of beryllium carbide with water. Both of the reactions produce methane and beryllium oxide or beryllium hydroxide. It is also possible that the gas bubbles are hydrogen produced by the reduction of water at cathodic sites on the beryllium. An image of these bubbles is shown in Figure 7.30.

![Figure 7.30 Image of the beryllium sample exposed to chloroform immersed in 30 ml of DDI water.](image)

In addition to the image of the gas bubbles on the beryllium chloroform sample, further images were collected of each of the samples after 30 days submerged in DDI water. These are shown in Figure 7.31. These images were taken while the sample was still within the glovebox on aluminium foil. The sample exposed to chloroform is shown in (a), the water in this beaker showed a slight colour change and significant amounts of gelatinous, aggregated, material highlighted in the figure with red arrows. The sample exposed to pentachlorobenzene and the clean sample are shown in (b) and (c) respectively. The images show the water to be clear. No signs of the material observed in the water for the chloroform sample appeared for these two samples. The water was not chemically tested to confirm the presence of beryllium because of the inherent high risk of exposure to the hydroxide.
Representative RLM images of the sample surfaces from the chloroform, pentachlorobenzene and clean sample surfaces are shown before immersion in DDI water, column 1. The surfaces of the chloroform (a) and clean samples (g) appear the same as the as polished beryllium surface. The sample exposed to pentachlorobenzene (d) shows solidified solvent droplets covering the sample surface. The samples were imaged again after 15 days immersion. These are shown in column 2. The sample exposed to chloroform (b) showed the presence of two defined corrosion pits after 5 days and the general surface appeared to be covered with a layer of contamination material, which could have possibly been corrosion products such as beryllium hydroxide. Scratches in the metal surface appeared to be highlighted by the presence of small pits. The pentachlorobenzene sample (e) appeared the same although angular features were observed underneath the solidified solvent droplets. It was not clear if these were corrosion phenomena or an effect of the droplets on the surface. The clean sample (h) showed no apparent change across the entire surface but a single pit was observed after 10 days, this is shown in Figure 7.33 (d).
The samples were examined again after 30 days of immersion and the images collected are shown in column 3. The surface of the chloroform sample (c) appeared to have been etched with the removal of surface material, indicating significant corrosive attack. Upon removing the sample from the water for imaging, a gelatinous material was observed on the side of the specimen, as it dried this turned white. This material was likely to have been beryllium hydroxide. The pentachlorobenzene sample (f), showed the same dark features below the solidified droplets but no differences were observed in their size, shape or structure. No film of material was observed on the surface of this sample as was observed on the chloroform exposed sample. The clean sample (i) appeared to be covered with a thin film of material as was observed on the sample exposed to chloroform after 5 days. The single pit that was observed also appeared to have increased in size.

In addition to the images collected in Figure 7.32, higher magnification images were collected of features of interest on each of the samples. Shown in Figure 7.33 are the features of interest. The two types of pits that were observed on the chloroform sample are shown in (a and b). The first type (a) appeared to be an anodic particle. An interference pattern is observed surrounding the particle, as was the case with some of the inclusions in Chapter 6. Additionally, a significant amount of corrosion products are observed at the interface of the particle with the matrix. The second type is shown in (b), here no inclusion was observed. Instead a large circular pit, with corrosion products at the pit mouth was observed. A white material was observed in the centre of the pit, which was thought to have been beryllium hydroxide. The cause of the pit was believed
to have been a carbide inclusion which had undergone hydrolysis, resulting in beryllium hydroxide and an empty hole.

The pentachlorobenzene sample showed dark jagged features, highlighted by the white arrows in (c). These appeared to be underneath the solvent droplets after each immersion stage. They did not appear to change with increasing immersion time. A single pit was observed on the clean sample following 10 days of immersion, this pit is shown in (d). The pit was located by observing the interference pattern at the interface of the matrix and the inclusion. The inclusion showed the deposition of corrosion products at this interface as the immersion time continued. This behaviour was consistent with the ceramic inclusions in Chapter 6, which showed crevice corrosion.

7.8 Discussion
7.8.1 Role of inhibitors in solvents
A number of additional constitutes are found in cleaning solvents designed for vapour degreasing. The solvents used in this project were the highest commercial purity that was readily available. A number of the solvents contained stabilisers and it was not possible to readily purchase these solvents without their addition. Of the solvents used in this work chloroform had ~1% ethanol added, dichloromethane had 50 ppm of amylene added and 1,1-dichloroethene had 200 ppm of MEHQ added. These are all added as solvent stabilisers.

Solvent stabilisers are grouped into five categories, these are: antioxidants, light inhibitors, thermal stabilisers, acid acceptors and metal inhibitors [116,121]. The purpose of each of these is to prevent reactions between the metal surface and the solvent.
Antioxidants are added to inhibit the formation of oxidation products generated by ultraviolet light or heat. They help suppress the free radical decomposition of solvents containing unsaturated functional groups by forming more stable resonance hybrids with the radical. These slow the catalytic oxidation of the solvent molecules and typically include amines and phenols. From the six solvents used in this work tetrachloroethene and 1,1-dichloroethene would be susceptible to oxidative attack. Tetrachloroethene would be more susceptible because of the higher boiling point of the solvent.

![Figure 7.34 Schematic to highlight how a radical is stabilised by resonance in an aromatic ring.](image)

Oxidative attack can be accelerated by light and so light inhibitors are also added to solvents that are susceptible to this form of degradation. Light inhibitors are typically long chain unsaturated organic molecules able to absorb high energy ultraviolet light photons preventing photolysis of the solvent molecules. The thermal stabilisers are similar to antioxidants as they are organic molecules with unsaturated functional groups which help to maintain the integrity of the solvent by competing with the solvent for reaction with free chlorine. Most chlorinated solvents are resistant to thermal breakdown at the temperatures used for vapour degreasing [116,122]. However, some solvents such as tetrachloroethene, which has a boiling point of 121.1 °C begins to thermally degrade at ~130 °C. When the solvent is overheated chlorine is liberated, eventually forming hydrochloric acid and a solvent dimer.

Acid acceptors or acid inhibitors act to neutralise the hydrochloric once it has been formed via the degradation of the solvent. It is particularly important in the design of solvents with an acid acceptor to ensure that the solvent is azeotropic, as the acid is most likely to form at the metal surface. The original method to neutralise the acid involved the addition of sodium hydroxide or sodium bicarbonate to the boiling solvent, however, modern additives are usually epoxides or amines. If the acid is not neutralised it can lead to the progressive breakdown of the solvent molecules. The scheme in Figure 7.35 shows how a modern epoxide inhibitor reacts with hydrochloric acid to remove the damaging acid species.

![Figure 7.35 Schematic of the reaction between an epoxide and hydrochloric acid to form a non-aggressive alcohol.](image)
Metal inhibitors are Lewis bases that inhibit solvent degradation in the presence of the metal and the salt. They deactivate reactive sites on the metal by either reacting directly with the exposed metal, to form an insoluble deposit or by complexing the metal salt. Both routes act to prevent further solvent degradation by forming a physical barrier between reactive species and the solvent.

It is recommended that any stabilisers added to chlorinated solvents will still result in an azeotropic solvent to prevent reactions between active metal surfaces and solvent molecules during degreasing. An azeotropic solvent ensures that the inhibitors are present in the vapour and not trapped in the boiling solvent below. As shown in Table 7.16, the boiling point of chloroform is ~17 °C lower than that of ethanol. This indicates that the vapour phase of the boiling solvent would not be azeotropic. This is the case because an azeotropic mix of these two liquids is 7 wt.% ethanol. As such, when the sample was exposed to the chloroform solvent vapours the ethanol stabiliser would have been present at the metal surface at a much lower concentration than the metal surface of the sample that was submerged for 30 days. This would prevent it from actively protecting the metal during degreasing but not during submersion.

Dichloromethane contains 50 ppm of amylene as a stabiliser. The amylene (1-pentene) has a boiling point slightly below that of dichloromethane. Literatures values for the azeotropic mix of these two could not be found. However, based upon the relative boiling points amylene should be present in the solvent vapours and at the metal surface during degreasing. The presence of amylene in the vapour phase may have acted to reduce the concentration of chloride formed at the metal surface for this sample.

1,1-Dichloroethene contained 200 ppm of monomethylether hydroquinone (MEHQ), this acts as a radical stabiliser through the resonance of the phenol group, reacting with any free chloride radicals in solution, preventing the reaction between the metal surface and the free chloride. Literatures values for the azeotropic mix of these MEHQ and 1,1-dichloroethene could not be found. However, based upon the relative boiling points MEHQ is unlikely to be present at a suitable concentration at the metal surface during degreasing so as to prevent chloride formation.

The original literature describing the thermodynamic modelling of solvents did not indicate which of the dichloroethene isomers were modelled. Three isomers of the molecule exist these being: 1,1-dichloroethene, trans-1,2-dichloroethene and cis-1,2-dichloroethene. E isomers are typically more stable than Z isomers. This is because the large side groups are further apart and do not interfere with each other in the E isomer and have a much lower potential energy. As noted by examining the compositions of the commercial cleaning solutions, the more sterically favourable trans isomer is used in these formulations. This suggests
that the structure of the solvent molecule is an important consideration for the formation of inorganic chlorides on metal surfaces. The difference in the behaviour of the solvent isomers is to be investigated in further work by a final year MEng student in 2016.

The commercial cleaning solvents generated the least, or possibly no, metal salts on the beryllium metal surfaces. The cleaning solutions are designed to be fully azeotropic with all solution components, ensuring that even on the hot metal surface, where the solvent vapour condenses, they are present and not left in the boiling solvent below. Following discussions with the solvent manufacturer HFE 71-DE and HFE 72-DE have a number of proprietary inhibitors added to the solvents that reacts with any free chlorine or fluorine in solution, preventing their reaction with a metal surface. These solutions have not previously shown any chloride or fluorine formation on aluminium or any other tested metals [123].

7.8.2 A mechanism for chloride formation on beryllium

Upon atmospheric exposure the free energy of a freshly cleaned metal surface is reduced by the formation of various layers. The native metal oxide will quickly acquire a layer of hydroxide, polar organic molecules, non-polar organics and finally an absorbed layer of gas. Each of these layers in turn reduce the free energy of the metal surface considerably [124]. The adsorbed hydroxyl groups present as part of the surface layering are known to be reactive sites on the metal oxide surface.

The structure of beryllium oxide is such that the \( \text{Be}^{2+} \) ion is surrounded in a tetrahedral arrangement of four \( \text{O}^{2-} \) ions forming a continuous network. At the surface termination of the oxide the hybridised \( \text{sp}^3 \) orbitals of the beryllium ion remain unfilled. This makes the beryllium ion electron deficient and able to act as a Lewis acid. Oxygen containing species present in the atmosphere or solution are to bond with these beryllium ions and be adsorbed onto the surface. The result is a surface film that can be considered as a partially hydroxylated beryllium oxide with a possible structure of \( \text{BeOOH}^- \).

The isoelectric point of beryllium oxide is \(~10.1\) as such when the surface is exposed to a neutral or acidic solution it will acquire a positive charge as per Equation 7.4:

\[
\text{Be}_{\text{oxide}}\text{OH} + \text{H}^+ \leftrightarrow \text{Be}_{\text{oxide}}\text{OH}_2^+ \quad (7.4)
\]

These positively charged adsorbed species can attract free chloride ions from solution as per Equation 7.5 or they may also attract solvent molecules as the lone pair of electrons from chlorine bonds to the surface resulting in adsorbed chloride containing species.

\[
\text{Be}_{\text{oxide}}\text{OH}_2^+ + \text{Cl}^- \leftrightarrow \text{Be}_{\text{oxide}}\text{OH}_2^+\text{Cl}^- \quad (7.5)
\]

The directly absorbed chloride ions and chlorine generated by the homolytic cleavage of the chlorine-carbon bonds in the solvent, can then be incorporated into the surface oxide film by traversing oxygen vacancies.
The resulting species from homolytic cleavage of the chlorine-carbon bonds are adsorbed chloride and a radical solvent species. If the solvent molecule contains two or more carbon atoms it can stabilise by forming sp^3 bonds with the rejection of a hydrogen ion. In the case of chloroform, the solvent molecule cannot lose a hydrogen ion to stabilise itself as such it will form a radical and remain unstable until a collision with another solvent molecule to form a dimer with the ejection of a hydrogen ion, as shown in Figure 7.36.

![Figure 7.36 Reaction scheme for the dimersiation of the solvent molecules generating hydrogen ions.](image)

The degradation of the solvent in this manner to form solvent dimers or alkenes with the generation of surface chloride has been shown for aluminium [115]. Although beryllium and aluminium are two and three valent ions respectively, they share a similar chemistry. It is reasonable to assume that similar reactions occur on the beryllium surface. Both metal chlorides are Lewis acids that are highly soluble in water, both metal ions are highly reactive and each metals has a passivating thin oxide layer.

**7.8.3 Investigating oxide dissolution**

Outlined in the previous section were the reactions that are believed to occur at the oxide surface that result in the degradation of the solvent. It has previously been suggested that these interactions between the reactive sites on the oxide and chlorinated solvents leads to dissolution of the oxide. A reaction scheme is proposed that may indicate how the oxide could be attacked. Although the equilibrium is likely to be far to the left, beryllium hydroxide that is present at the oxide surface, undergoes a reversible dissociation reaction. This produces hydroxyl groups and the lattice cation ion Be(OH)^+ as per Equation 7.4. This can then react with chlorine via the donation of electrons to the unoccupied orbital on the beryllium ion forming beryllium hydroxychloride, as per Equation 7.5.

\[
Be(OH)_2 \leftrightarrow Be(OH)^+ + OH^- \quad (7.4)
\]

\[
Be(OH)^+ + Cl^- \rightarrow BeOHCl \quad (7.5)
\]

The vacant sp^3 orbitals on the beryllium ion may then be filled by electron donation from the chlorine atoms present in the solvent molecules. The resulting solvent complex may then be soluble in the solvent as is the case with aluminium complexes which produce a red colour upon formation. The formation of a coloured complex after scribing beryllium was not observed.

To investigate if there was any evidence for a change in the oxide thickness, it was calculated at each stage of the experiment. Shown in Table 7.17 are the values for the oxide thickness calculated at each stage of the instigation for all of the samples exposed to the solvents including the samples scribed under the solvent and the two samples exposed to the commercial cleaning solutions. There is no general trend observed to indicate that the oxide is dissolved upon exposure to the chlorinated solvent vapours. Despite showing the highest
concentration of chloride, the sample exposed to chloroform showed no apparent change in the oxide thickness and oddly the sample that showed the least chloride formation experienced a slight drop in the oxide thickness. As a consequence of the metal and oxide peaks being close in kinetic energy the often used equation enabling an approximate correction of the peak intensities for a carbon over layer would not change the ratio between the peaks and hence the oxide thickness.

Table 7.17 Oxide thicknesses at each stage of the experiment from all of the samples that were investigated. (s) scribed while submerged under the solvent

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial</th>
<th>Solvent exposed</th>
<th>Change</th>
<th>Rinsed</th>
<th>Change</th>
<th>Overall change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>2.62</td>
<td>2.62</td>
<td>0.00</td>
<td>2.53</td>
<td>-0.09</td>
<td>-0.09</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>2.75</td>
<td>2.60</td>
<td>-0.15</td>
<td>2.73</td>
<td>0.13</td>
<td>-0.02</td>
</tr>
<tr>
<td>Tetrachloroethene</td>
<td>2.67</td>
<td>2.73</td>
<td>0.06</td>
<td>2.58</td>
<td>-0.15</td>
<td>-0.09</td>
</tr>
<tr>
<td>1,1-Dichloroethene</td>
<td>2.68</td>
<td>2.70</td>
<td>0.02</td>
<td>2.50</td>
<td>-0.20</td>
<td>-0.18</td>
</tr>
<tr>
<td>Pentachlorobenzene</td>
<td>2.54</td>
<td>3.73</td>
<td>1.19</td>
<td>3.74</td>
<td>0.01</td>
<td>1.20</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>2.53</td>
<td>2.68</td>
<td>0.15</td>
<td>2.80</td>
<td>0.12</td>
<td>0.17</td>
</tr>
<tr>
<td>Chloroform (s)</td>
<td>2.62</td>
<td>4.42</td>
<td>1.80</td>
<td>-</td>
<td>-</td>
<td>1.80</td>
</tr>
<tr>
<td>Dichloromethane (s)</td>
<td>2.75</td>
<td>4.57</td>
<td>1.82</td>
<td>-</td>
<td>-</td>
<td>1.82</td>
</tr>
<tr>
<td>HFE 71-DE</td>
<td>2.85</td>
<td>2.52</td>
<td>-0.33</td>
<td>2.87</td>
<td>0.35</td>
<td>0.02</td>
</tr>
<tr>
<td>HFE 72-DE</td>
<td>2.72</td>
<td>2.93</td>
<td>0.21</td>
<td>2.69</td>
<td>-0.24</td>
<td>-0.03</td>
</tr>
</tbody>
</table>

However, it is possible to qualitatively explain the effect of the changing carbon thickness on the oxide thickness. A significant change in the apparent thickness of the surface oxide was observed for the sample after being exposed to pentachlorobenzene. This was a result of the solvent layer adhered onto the surface. This layer will attenuate electrons from the metal to a greater extent than the electrons from the oxide, thereby reducing the metal peak intensity relative to the oxide peak intensity. This would give the expected result of an increase in the oxide thickness. Even accounting for the slight increase in the carbon concentration and the extra attenuation of metal electrons, the results still do not indicate oxide dissolution. For example, for the chloroform sample, the initial oxide thickness was 2.62 nm and after solvent exposure it was 2.62 nm, no change in thickness but this is also accompanied by a drop of 7.4% in the carbon concentration. This drop should have the effect of decreasing the effective oxide thickness, which would make the oxide thicker after solvent exposure which is not shown by the results that were obtained.

Despite taking the effects from the changing carbon over layer into account their appeared to be little evidence for oxide dissolution caused by a reaction between the oxide and the solvent during vapour degreasing. However, it should be noted that the error in the equation for calculating the oxide thickness is at least ±10% [119]. Additionally, the take off angle (θ) is poorly defined in the Theta Probe spectrometer as the transfer lens has a cone angle of 50°. It is more defined for the ESCALAB which has a cone angle of 20°, resulting in more accurate oxide thickness values for the samples that were not scribed.

### 7.8.4 Accelerated corrosion

It was believed that the chloride formed at the surface of beryllium could act as a corrosion precursor as when the sample was exposed to moisture, hydrochloride acid would be generated. It is possible to estimate the amount of chloride on the sample and hence the concentration of chloride ions present in solution. The total surface area of the beryllium sample was ~268 mm$^2$. If it is assumed that, based on a chloride concentration...
concentration of 1 at.% that the thickness of beryllium chloride is about a monolayer and the atomic surface density of beryllium is \( \sim 1.6 \times 10^{19} \) atoms m\(^{-2}\) based upon the average of the three single crystals, as shown in Chapter 2. This equates to \( \sim 4.3 \times 10^{15} \) atoms at the surface of the beryllium. Assume that every beryllium atom is bound to one chlorine atom, resulting in \( 7.1 \times 10^{9} \) moles of chlorine. Resulting in a solution concentration of \( 2.38 \times 10^{-7} \) mol dm\(^{-3}\) in the test beaker.

Despite the low concentration of chloride in solution, it appeared as if the beryllium sample that was exposed to chloroform did undergo accelerated corrosion. Pitting was observed within 5 days and corrosion products were observed across the entire surface of the sample. Additionally, beryllium hydroxide was observed on the sides of the sample as were gas bubbles when the sample was left in solution. These are indicative of active corrosion processes.

Oddly little corrosion was observed on the surface of the pentachlorobenzene sample. This was thought to be a consequence of the solidified droplets of solvent on the surface. A suitable solvent could not be found that was capable of dissolving pentachlorobenzene from the sample surface. As such it was not possible to examine the surface for signs of corrosion underneath the solidified solvent droplets.

### 7.9 Conclusions

The results generally agreed with the thermodynamic modelling. It was previously concluded that solvents selected for use with beryllium should have a low carbon atom content and a high H:Cl ratio. Two relationships for the carbon content were observed. For those solvents predicted to form chloride: less carbon produced more chloride. However, for those solvents not predicted to form chloride: less carbon produced less chloride. It appeared as if the H:Cl ratio played a more important role in chloride formation than the number of carbon atoms in the solvent molecule.

For the solvent pairs with the same carbon content but different H:Cl: chloroform - dichloromethane and tetrachloroethene - dichloroethene the difference in chloride was 1.12 at.% and 0.38 at.% for each pair respectively. For the solvent pairs with almost the same H:Cl but different carbon content: chloroform - tetrachloroethene and dichloromethane - dichloroethene the difference in chloride was 0.58 at.% and 0.16 at.% for each pair respectively. The experimental results obtained herein support the conclusion that a solvent containing a low number of carbon atoms and a relatively high H:Cl ratio should be used with beryllium.

The samples cleaned using the commercial cleaning solvents, designed to replace older chlorinated solvents, showed significantly less chloride formation. The lowest concentrations of chloride were observed on the samples exposed to these solvents. It is possible that, because of the poor signal to noise in the spectra together with the initial concentration of chloride and fluoride that no chloride or fluoride formation occurred on the surfaces of the samples exposed to these solvents.
The main aim of the project was to understand more about the microchemistry associated with the second phase particles and corrosion of beryllium, as such a novel experimental technique and methodology was developed. It is hoped that this technique will enable the acquisition of chemical state information from the surfaces of small surface features in the micron and sub-micron regime. The initial proof of concept and results from this method are outlined in the next chapter.
8.1 Introduction

In this thesis the role of second phase particles in the localised corrosion of aluminium and beryllium has been examined using various analysis techniques. These techniques have provided some chemical but mostly elemental information about the oxide film on second phase particles and their associated corrosion products. To explore the possibility of obtaining more in depth chemical information from these, a new experimental methodology and surface analysis technique was developed and is described in this chapter.

AES and XPS have historically provided different information about a sample. If information at high spatial resolution is required AES is utilised. However, if chemical state information is needed XPS is used. Modern XPS instruments have shown improvements in spatial resolution but there is still a vast difference in spatial resolution between these techniques. AES is considered to be a 10-100 nm technique while XPS is typically in the 10-1000 μm regime.

Typical photoelectron analysis uses a spot size of ~400 μm, decreasing to ~15 μm when utilising the smallest achievable spot sizes. Although in parallel imaging mode, this can be further reduced to ~3 μm. The spatial resolution of AES has also improved achieving 8 nm in AES mode and 3 nm in SEM mode. AES is also able to provide some chemical information for certain elements; the majority of these are the light metals/metalloids such as lithium, beryllium, aluminium and silicon. For the most part, transition metals do not show detectable shifts, when they change chemical state. The common notable exceptions are copper and zinc. Although in some cases the peak shape can be used to infer chemical information.

Despite the advances in XPS spatial resolution, the analysis of individual micron sized features cannot be achieved using XPS, only an averaged spectrum from an array of features can be obtained. Either the averaged data must be used or the user must suffice with the limited information from AES analysis. An ideal technique would enable chemical state information, from any element of interest, to be obtained from individual sub-micron features. Proximal XPS is a technique that could achieve this. Proximal XPS avoids the problem of focusing x-rays into a small spot by generating the x-rays right next to the region of interest.

8.2 Literature review

Previous investigations using locally generated x-rays for the excitation of photoelectrons have been performed using a cylindrical mirror analyser (CMA). The first attempt to utilise locally excited x-rays examined the ability to analyse thin films deposited onto an x-ray producing substrate. The instrument that was designed came in the form of an inverted CMA that was mounted below the sample. A schematic of the setup is shown in Figure 8.1. By rastering an electron beam on the reverse side of a sample, mounted on an x-ray source material, it was possible to generate x-rays within the foil that would then excite photo and Auger electrons from the thin foil sample. These could then be detected by the CMA. Although the technique produced suitable spectra for general analysis, it did not enable the extraction of chemical information from
the spectrum. The technique was limited by the inherent low spectral resolution of the CMA. As noted in
Chapter 3, this type of analyser design is not suitable for collecting Auger spectra with the high energy
resolutions, <0.05%, required for chemical state analysis.

![Schematic of the experimental setup for local x-ray excited photoelectrons from thin films. Scheme reproduced [125].](image)

It was not until the CMA was replaced with a hemispherical sector analyser (HSA) that the technique became
viable for assessing chemical states. By replacing the CMA with a HSA in the same transmission setup,
chemical state information could be extracted from microtomed samples of an interface between an adhesive
and a coating, which were deposited onto aluminium foil. The resulting photoelectron spectra had a
resolution comparable to the photoelectron peaks generated using an achromatic x-ray source [126]. An
important conclusion of the work on thin foil x-ray sources was the need to adjust the electron beam energy
such that the interaction volume was isolated to the foil. By isolating the electron cascade to the foil the
maximum intensity of x-rays are produced for sample analysis. The resultant spatial resolution was then
proportional to the x-ray interaction volume and was ~1 μm.

An important consideration for the technique of local x-ray excitation is that the characteristic x-ray line
width of the source must be low. If the line width is too large, sufficiently high spectral resolutions cannot be
obtained for probing chemical states. This limits the choice of x-ray source to aluminium, magnesium or
silicon [127]. To locate and successfully analyse surface features of interest, a transmission form of local x-
ray generation is unsuitable. Instead the technique needed to be further developed to allow imaging of the
surface, selection of the desired area for analysis and obtain surface chemical state information from a region
as small as possible, ideally <1 μm.

### 8.3 Initial investigation into the use of proximal XPS

The initial proof of concept study was performed by Dr. Rossana Grilli in 2011 using a copper transmission
electron microscopy (TEM) grid supported on an aluminium substrate. In this work an aluminium SEM
sample support stub was wet ground and polished to a 1 μm diamond finish. A copper TEM grid was placed
on the stub and the sample was moved to the MICOLAB 350. The TEM grid contained a fine mesh of 80 μm
holes, as shown in Figure 8.2.
Then a fine copper splinter protruding from the edge of one of the copper struts was located using the SEM. The electron beam was aligned onto the substrate and located ~50 nm from the splinter. The beam energy was increased to 15 keV, the aperture for the SEM was removed and the kinetic energy range 530-570 eV was scanned to acquire the Cu 2p transitions. Removal of the SEM aperture increased the sample current from ~5 nA to ~50 nA. A noticeable set of two peaks was observed within 5 minutes of signal acquisition. Analysis was continued for ~1 hour to collect the spectrum shown in Figure 8.3. This spectrum shows the raw as-collected data. Two peaks corresponding to the Cu 2p\( _{3/2} \) and the Cu 2p\( _{1/2} \) photoelectron peaks are observed on the steep rising background.

The raw data is converted to a binding energy scale by correcting for excitation using Al K\( \alpha \) x-rays of energy 1486.68 eV. The Cu 2p\( _{3/2} \) peak has a binding energy of ~933 eV and correcting this for the kinetic energy of the aluminium photon, 1486.68 eV, places the Cu 2p\( _{3/2} \) peak at ~554 eV on the kinetic energy scale. A linear background subtraction was also performed to remove the steep rising background of the AES spectrum. Figure 8.4 shows the resultant spectrum. Although noisy, the spectrum can clearly be identified as the Cu 2p region, containing the Cu 2p\( _{3/2} \) and Cu 2p\( _{1/2} \) photoelectron peaks, with a separation of ~20 eV, which is expected for copper. Close examination of the spectrum shows a small feature at ~943 eV which could be a weak shake-up satellite.
Figure 8.4 High resolution Cu 2p spectrum after correcting for binding energy and removing a linear background from the raw data.

Figure 8.5 shows the smoothed (Savitzky–Golay filter [128]) spectrum illustrating no loss of spectral information upon smoothing. The small feature at ~943 eV is more clearly observed and was located at the binding energy expected for the large shake-up of CuO. The weak peak intensity would suggest the oxide has been mostly reduced. The feature to the lower binding energy side of the Cu 2p3/2 may be the Kα3,4 satellite of the peak.

8.4 Experimental development

8.4.1 Selection of sample

The original proof of concept investigation was expanded to look at smaller features of interest, in particular individual small particles. Particles were selected instead of small surface features as their size and composition could be easily controlled and they were readily available. Copper particles obtained as precipitated powder (BDH Laboratory Supplies >99.5%) were chosen as a starting material.

8.4.2 Instrument setup for analysis

To maximise the signal intensity of the photoelectron peak in the AES spectrum the use of sample tilting was investigated. In order to study the effect of tilting the sample towards the analyser transfer lens, the sample
was excited using a 1.5 keV primary beam energy. This enabled the backscattered peak to be used as an analogue for the photoelectron peak. The backscattered peak was used because it was intense and could be reliably monitored. The low primary beam energy was used in order to allow the backscattered peak to be analysed as the analyser is only capable of analysing electrons up to ~2500 eV in kinetic energy. Figure 8.6 shows how the intensity of the backscattered peak changes with tilt angle. The intensity increases as the tilt angle approaches 60°. At 60°, the sample is perpendicular to the transfer lens and normal electron emission occurs. Tilting further than 60°, to 70° and 80° led to a reduction in intensity. Figure 8.7 shows a schematic which helps illustrate the various angles involved in the analysis.

Figure 8.6 High resolution electron spectrum of the backscattered peak intensity as a function of sample tilt angle.

Although tilting the sample does lead to an increase in the size of the electron beam spot at the sample surface, this was not understood to be an issue as the excitation envelope of the primary beam was more than 50x greater than the extended spot size. With a 0° tilt or horizontal surface, the spot size was ~20 nm. With a 40° tilt the spot size was ~26 nm and the peak intensity was increased by 100%. When the sample was tilted to 60°, the spot size was ~40 nm and the peak intensity increased by 130%.

Figure 8.7 Schematic to illustrate the various angles involved in the sample setup for proximal XPS analysis.

Although tilting to 60° provided the maximum signal intensity, the tilt angle that was eventually chosen was 40°. This was because channeltron saturation with the associated peak inversion was observed in survey spectra collected from samples when tilting to 60°. Figure 8.8 shows an example of this peak inversion.
While the C KLL and O KLL remain unaffected, the Al KLL at ~1400 eV appears to decrease in intensity and invert at the point of maximum intensity. This is indicative of the channeltrons becoming saturated with too many incoming electrons and is unable to correctly count them all. The count rate for the Al KLL transition in the spectrum exceeds $3.5 \times 10^6$ counts s$^{-1}$, which is extraordinarily high compared to the count rates encountered in typical analysis. When the sample is tilted to 60°, such that the sample normal is along the analyser axis there is also a risk of reflecting the backscattered peak into the detector, resulting in damage to the electronics.

![Survey spectrum from an aluminium substrate tilted to be normal to the transfer lens of the electron analyser.](image)

The final experimental setup within the instrument analysis chamber is shown in Figure 8.9. Particles of interest were deposited onto a clean smooth substrate. Ideally the particles should not be deposited too closely to one another such that the signal from multiple particles could interfere with one another, this is discussed in a later section. Particles are then located on the surface using low sample current, 5 nA, SEM imaging in the Auger microscope. This is performed using gun aperture one and a beam energy of 15 keV. Once a particle of interest was identified the sample was tilted 40° from the sample normal to align more closely with the analyser acceptance lens. The electron beam was placed off of the particle of interest and then the SEM gun aperture was removed to maximise the sample current to ~50 nA. Acquisition of photoelectron spectra was then carried out.
By performing a Phi-Rho-Z simulation using a 15 keV beam energy and an aluminium substrate it is possible to estimate the size and shape of the envelope for generation of the Al Kα as shown in Figure 8.10. This then allowed the electron beam to be placed in a position such that the particle was exposed to a good proportion of the generated x-rays.

8.4.3 Minimum distance between two particles

In order to estimate the minimum distance that particles could be separated from each other without causing cross interference, AES line scans were performed leading away from a particle. The Cu L₃M₄₅M₅₅ Auger was used as an analogue for the photoelectron peak as it was more intense. By recording the intensity of the Auger, as a function of distance from the particle, it was possible to estimate the minimum distance that particles could be separated from one another without cross interference.

To estimate the minimum distance between features, the system was setup in the same manner as previously described. A 4 µm long line scan, divided into twenty analysis points with a step size of ~210 nm was
performed. At each point the Cu $L_3M_{4,5}M_{4,5}$ Auger region was collected. Figure 8.11 shows the line scan leading away from the copper particle.

Figure 8.11 SEM micrograph of a small copper particle on an aluminium foil with the with the 4 μm line scan highlighted.

By measuring the intensity of the Auger peaks, after performing a linear background subtraction, it was possible to estimate the peak intensity at each distance along the line. Figure 8.12 shows the results of this the line scan. The graph shows how after 3.5 μm to 4 μm away from the particle the intensity of the Auger and therefore the photoelectron peak, would be so small that it would not significantly interfere with the signal generated from the particles of interest. A minimum recommended distance between particles would therefore be ~4 μm.

Figure 8.12 Graph of the copper Auger intensity recorded from a line scan with increasing distance away from a particle.

**8.4.4 Optimisation of the electron beam position**

In order to align the electron beam to the ideal position for analysis, the EDX detector attached to the microscope was utilised. Analysis points were placed in a line away from the particle with a spacing of ~100 nm. The position, at which the Cu $L_α$ x-ray peak was no longer observed in the EDX spectrum, was taken as the ideal position for the beam. The absence of copper x-rays at this point shows that the electron beam is no longer striking the particle. When the gun aperture is removed the sample current increases significantly. This is caused by the increase in the flux of electrons hitting the sample. Without a collimating gun aperture many of these electrons fall out of the ideal beam position at the surface, resulting in a larger area of x-ray
The ideal position for the beam was found to be between points 8 and 9 in Figure 8.13. This corresponded to a distance from the particle of ~300-450 nm. The poor SEM image quality is a consequence of the high sample current.

![Figure 8.13 SEM micrograph of a copper particle with positions for EDX analysis marked leading away from the particle.](image1)

Although, Auger point analysis was initially used for acquiring spectra, it was observed that the use of point analysis caused drift of the small particles of interest. This may have been a consequence of the significant charge density of a single beam position. The point analyses were replaced with Auger area scans, each consisting of 200 nm square boxes. In the boxes the beam rapidly rasters over the entire boxed region which decreases the charge density of the signal generation region and helped to prevent drift of the particles. An example of this form of analysis is shown in Figure 8.14.

![Figure 8.14 SEM micrograph of a sub-micron copper particle imaged with maximum sample current. The boxes highlight the positions of AES analysis, where the electron beam is rastered inside the box.](image2)

### 8.4.5 Comparison with traditional XPS

The shake-up for copper (II) oxide was not observed in the proximal photoelectron spectrum collected from a number of copper particles. Therefore, to determine if there was a problem with localised heating and reduction of the particles, an array of copper particles dispersed on aluminium foil was analysed using traditional XPS. The RLM image from the surface is shown in Figure 8.15 with a highlighted region to show...
the size of the x-ray spot that was used. This shows that a large number of particles were included within the analysed area.

![RLM image of the aluminium foil surface with dispersed copper particles. Highlighted in light blue is the size of the x-ray spot used in XPS analysis, the centre of the oval shows a much smaller spot indicating the smallest achievable spot size with a laboratory based instrument.](image)

The high resolution Cu 2p spectrum from the array of copper particles is shown in Figure 8.16 (a). An intense divalent shake-up satellite was observed. To simulate the effect of sample reduction, the surface was lightly argon ion etched for ten seconds. The resultant Cu 2p spectrum is shown in Figure 8.16 (b). Etching, as expected, led to a significant reduction in the intensity of the shake-up. The resulting spectrum, looked similar to the spectrum collected from the single copper particles, as shown in Figure 8.17 (b).

![High resolution Cu 2p spectra collected from the array of copper particles using traditional XPS: (a) As-deposited and (b) after 10s of argon ion etching.](image)

**8.5 Results obtained using an aluminium substrate**

**8.5.1 First results from a copper particle**

The initial investigation focused on larger particles as it was thought that the larger particles would generate more photoelectrons as a greater surface area is available for their generation. An example of a large ~6 µm particle that was analysed is shown in Figure 8.17 (a). The spectrum collected from the region off of the particle “off” is shown in Figure 8.17 (b). The spectrum shows the Cu 2p region. The Cu 2p₃/₂ and the Cu 2p₁/₂ peaks are clearly observed above the background. The spectrum has been corrected to a binding energy scale and a linear background subtraction has been performed.
Figure 8.17 (a) SEM micrograph of the copper particle from which the first proximal XPS spectrum was collected. (b) High resolution Cu 2p spectrum collected from the 6 μm particle. The spectrum shown was corrected for binding energy and a linear background was removed from the raw data.

To fully assess the potential of the technique and to test the smallest features that could be analysed, a small sub-micron particle was located on the aluminium substrate. The smallest particle that could be located is shown in Figure 8.18 (a). It was ~700 x 500 nm. The long thin inclusions seen in the figure are copper intermetallics. The survey spectrum collected from off of the particle is shown in Figure 8.18 (b). The spectrum shows intense Cu LMM Auger transitions from the particle in addition to an intense Al KLL transition from the substrate. The position in the survey spectrum where the copper photoelectron peak occurs has been highlighted. The copper photoelectron peak collected from the same spot is shown in Figure 8.19. The spectrum is similar to the spectrum acquired from the larger particles, although it has a poorer signal to noise.

Figure 8.18 (a) SEM micrograph of the first sub-micron copper particle analysed by proximal XPS and (b) AES survey spectrum collected from off of the copper particle.
Chapter 8

Proximal XPS

Christopher F. Mallinson

Figure 8.19 High resolution Cu 2p photoelectron spectrum collected in the electron microscope. The spectrum shown was corrected for binding energy and a linear background has been removed from the raw data.

It was decided that because the $2p_{3/2}$ transition is twice as intense as the $2p_{1/2}$ transition, it would be more efficient to acquire the more intense $2p_{3/2}$ instead of trying to capture the entire 2p region. The later results for copper particles show only the Cu $2p_{3/2}$ peak.

8.5.2 First results from an iron particle

Once the experimental setup was shown to work for copper particles, the investigation was expanded to include other metal particles. Iron and nickel particles were analysed and in both cases successful identification of a photoelectron peak was achieved. Figure 8.20 (a) shows an iron particle deposited onto the aluminium substrate. The point marked “off” shows the position of the electron beam for photoelectron excitation. Figure 8.20 (b) shows the survey spectrum collected from the surface near the iron particle. The spectrum is consistent with the spectrum recorded from the copper particle on an aluminium substrate, except that Fe $LMM$ Auger transitions are now observed. Intense O $KLL$ and Al $KLL$ peaks are observed from the substrate. These peaks are observed as a result of internal scattering of the primary electrons within the particle. These scattered electrons are emitted onto the substrate and excite Auger electrons from the substrate [129]. The position at which the iron photoelectron appears in the spectrum has also been marked.

Following the acquisition of the survey spectrum the iron photoelectron peak was acquired. Figure 8.21 (a) shows the high resolution spectrum of the Fe 2p region. Figure 8.21 (b) shows the same region, corrected to a binding energy scale and following a linear background subtraction. The spectrum showed a narrow peak in the expected position for the Fe $2p_{3/2}$ in addition to two broader peaks. An initial theory regarding the identity of the peaks next to the Fe $2p_{3/2}$, was the possibility of charging artefacts from interactions between the oxide layer on the particle and the oxide layer on the aluminium substrate. Therefore, the sample was heavily argon ion etched for 10 minutes until no trace of oxygen was observed in the AES spectrum on or in the vicinity of the particle.
Further point analysis and high resolution spectra of the Fe 2p region still showed the presence of the additional peaks. EDX was performed on the sample stub and revealed that it contained ~4 at.% of copper. This was present in the form of intermetallics. The two broad peaks observed at the higher binding energy side of the iron peak were the 1D and the 3P Cu L\textsubscript{3}M\textsubscript{2,3}M\textsubscript{2,3} transitions. The peak overlap demonstrates the need, as with traditional XPS, for a multiple anode system so that Auger peaks can be away from the photoelectron peaks of interest.

8.5.3 Analysis of an intermetallic

To expand upon the initial work investigating small particles, the photoelectron peaks from intermetallics and inclusions were investigated. It was decided to analyse the copper intermetallics present in the aluminium SEM stub. A large copper intermetallic, shown in Figure 8.22, was selected from a fairly clear region of the surface. The high resolution Cu 2p\textsubscript{3/2} photoelectron spectrum collected from the “off” position of the intermetallic is shown in Figure 8.23. The signal to noise is poor because of the low spectral acquisition time that was used. This was because of instrumental time demands.
The results from the intermetallic highlight the use of the surrounding substrate as the x-ray source for looking at a surface feature. An inherent problem with this form of proximal XPS would be the limited materials that make suitable x-ray anodes. Aluminium and magnesium anodes are most widely used in laboratory XPS instruments because of the narrow energy range of the $K\alpha_{1,2}$ x-ray transition. Silicon is also a useable anode albeit with a slightly wider $K\alpha_{1,2}$ distribution. Most elements are not suitable local x-ray sources for XPS. For instance, Be $K\alpha$ x-rays, with a kinetic energy of ~110 eV, would provide an excellent way to probe the low binding energy 3d shells of transition metals because the excitation cross section would be particularly large. However, they have a wide energy distribution and the FWHM of Be $K\alpha$ is ~5 eV. The use of these x-rays would result in a loss of all chemical information from the resulting spectrum.

### 8.6 Results obtained using a magnesium substrate

#### 8.6.1 Results from copper particles and the effect of particle size

During the analysis of copper particles on the magnesium surface, an intriguing effect was observed. Counter-intuitive to the expected results, smaller particles appeared to produce spectra of better quality, with an improved signal to noise, compared to the spectra collected from larger particles. The SEM micrographs...
of three different sized copper particles (a, b and c), on magnesium are shown in Figure 8.24. They are approximately 10, 4 and 1 μm in size respectively.

![Figure 8.24 SEM micrographs of three different sized copper particles on magnesium, (a) 10 μm, (b) 4 μm and (c) 1 μm. Together with the high resolution Cu 2p\(_{3/2}\) spectra collected from each of them, (d, e and f) respectively.](image)

The high resolution Cu 2p\(_{3/2}\) spectra from each of the particles are shown in Figure 8.24 (d, e and f). They show that the signal to noise in the spectrum improves as the particle size decreases. An explanation for this is thought to be that because the x-rays used for generating the photoelectrons are flooding the particles from beneath the surface, larger particles will attenuate more of the x-rays and so photoelectrons would not be produced from the entire particle surface. X-rays flooding the smaller particles completely envelope the particle and allow for photoelectron emission from their entire surface, resulting in a more intense signal. Results from Phi-Rho-Z simulations show that >95% of the Al Kα x-rays traversing through copper are absorbed within 300 nm of material, with 50% absorbed within 100 nm of material. A graphical representation of the modelled depth is shown in Figure 8.25 although the curve shows the region from...
which x-rays are emitted within a material it can also be interpreted as an estimation for the maximum depth of penetration by the x-rays in a copper substrate.

This indicates that the highest quality spectra would be obtained for copper particles smaller than 300 nm. The analysis times for the spectra shown in Figure 8.24 were all ~20 minutes.

**8.6.2 Results from an iron particle**

After identifying the two Cu $L_3M_{2,3}M_{2,3}$ Auger transitions overlapping the Fe 2p region when using the aluminium substrate, to analyse the iron particles, it was decided to try and use an alternative x-ray source. Iron particles were deposited onto a piece of magnesium foil for analysis. An example of an iron particle that was analysed is shown in Figure 8.27 (a). The survey spectrum collected from the particle is shown in Figure 8.27 (b). It shows that the particle is likely covered in a layer of iron oxide as the O $KLL$ is quite intense. It also shows that there is some internal scattering within the particle which causes Auger electrons to be excited from the magnesium substrate.

The high resolution Fe 2p$_{3/2}$ spectrum, collected from the sub-micron iron particle is shown in Figure 8.28. It shows the photoelectron region free of interference from the copper Auger peaks. On the magnesium substrate, the Fe 2p$_{3/2}$ photoelectron peak is located at a slightly lower binding energy than was observed on the aluminium substrate. This may be caused by some localised charging on the magnesium surface.
8.7 Substrate development

During the investigation it became apparent that the original polished aluminium SEM sample stub, as shown in Figure 8.29 (a) was not suitable for use as a substrate. The original stub was found to contain copper in the form of second phase intermetallic particles. An SEM micrograph of the polished surface is shown in Figure 8.29 (b). The bright objects are aluminium-copper intermetallics. It was thought that these intermetallics, as well as any copper in solid solution would have contributed to the intensity of the photoelectron peak. The aluminium x-rays excited within the substrate would be able to excite photoelectrons from the copper atoms present in solid solution in addition to those atoms in nearby intermetallics, resulting in a Cu 2p photoelectron peak from the substrate.

Not only was there an issue of the copper present in the aluminium substrate, it was also believed that there was a degree of beam induced damage effecting the particles. This was not caused by the beam dwelling on the particle but by the reduction of the surface oxide on the particles caused by the localised heating of the substrate. Table 8.1 shows the proximal XPS results from four different copper particles using the original substrate.
Table 8.1 Peak energies for copper particles analysed using an aluminium substrate

<table>
<thead>
<tr>
<th>Particle</th>
<th>Cu $L_3M_{2.3}M_{4.5}$ (KE/eV)</th>
<th>Cu 2p (BE/eV)</th>
<th>Modified Auger parameter $\alpha^*$ (eV)</th>
<th>Possible Cu oxidation states</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>917.2</td>
<td>934.5</td>
<td>1851.7</td>
<td>0 or II</td>
</tr>
<tr>
<td>2</td>
<td>917.9</td>
<td>934.0</td>
<td>1851.9</td>
<td>0 or II</td>
</tr>
<tr>
<td>3</td>
<td>917.6</td>
<td>934.4</td>
<td>1852.0</td>
<td>0 or II</td>
</tr>
<tr>
<td>4</td>
<td>917.9</td>
<td>934.0</td>
<td>1851.9</td>
<td>0 or II</td>
</tr>
</tbody>
</table>

The values for the Auger parameter of the four analysed copper particles are close to the reported value for copper II oxide, $\alpha^* = 1851.5$ eV. However, in none of the analyses was there significant evidence of the characteristic divalent shake-up satellite. Therefore, it was concluded that the particles must have been in the metallic state, $\alpha^* = 1851.2$ eV. This suggested that the particles were undergoing some degree of beam damage as copper is oxidised in air and carries a thin oxide layer.

Based upon these observations it was decided to attempt to use a stack of thin foils to help dissipate heat and remove the impurities found in the aluminium stub. Figure 8.30 (a) shows the next development in the sample substrate. The SEM stub was covered with stacked laboratory grade, 99.5 at.% aluminium foil, which was $\sim 12$ μm thick. The foil was folded onto itself twice to make a series of four aluminium layers. EDX of the foil revealed no impurities. However, during analysis an Auger peak in the copper photoelectron region was detected and determined to be the Mn $L_3M_{2.3}M_{4.5}$ Auger transition. This is shown in Figure 8.30 (b). The absence of the manganese signal in the EDX spectrum indicates that either the manganese was a surface contaminant or that the EDX analysis time was insufficient to resolve the peak above the noise.

The replacement foil contained impurities and did not appear to resolve the problem of particle reduction. Therefore, it was replaced with a higher-purity, thinner aluminium foil. The laboratory foil was replaced with $>99.91$ at.%, 0.8 μm thick, aluminium foil. The foil was folded over onto itself four times to create a layered structure. The edges of the stack were adhered to the sample stub with conductive silver paint, as shown in Figure 8.31.
8.8 Results from a copper particle following optimisation

The final results were collected following all of the previously mentioned optimisation steps. The substrate utilised was the thin, high purity, aluminium foil stack. The electron beam position was aligned using the Cu Lα x-ray peak, the point analysis was replaced with a rastered 200 nm box and the sample was tilted to 40°. Using this setup the spectrum shown in Figure 8.32 was collected, the figure shows the usual line spectrum presentation replaced with points. The spectrum shows two peak components. The lower binding energy peak is the Cu(I)O photoelectron peak and the higher binding energy peak is the Cu(II)O photoelectron peak. A Cu(II) shake-up satellite is also observed. The spectrum shows that the use of the optimisation steps led to an improvement in the beam induced reduction of the copper particle.

The results of the various particles studied in this work are summarised in Table 8.2. It shows the binding energies of the photoelectron peaks in addition to the kinetic energies of the primary Auger transitions. Modified Auger parameters have also been calculated for all of the particles.
Table 8.2 Results of the various particle analyses on different substrates before and after optimisation. The final copper particle shows values for both peak components

<table>
<thead>
<tr>
<th>Particle</th>
<th>Substrate</th>
<th>Size (μm)</th>
<th>Acquisition time (s)</th>
<th>Binding Energy Cu 2p⁰/² (eV)</th>
<th>Kinetic Energy Cu L⁰/M⁰,⁵ (eV)</th>
<th>Modified Auger parameter α* (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>Al</td>
<td>0.8</td>
<td>1800</td>
<td>934.2</td>
<td>918.0</td>
<td>1852.0</td>
</tr>
<tr>
<td>Cu</td>
<td>Mg</td>
<td>30</td>
<td>1500</td>
<td>934.0</td>
<td>918.0</td>
<td>1852.0</td>
</tr>
<tr>
<td>Cu</td>
<td>Mg</td>
<td>10</td>
<td>1500</td>
<td>934.0</td>
<td>918.3</td>
<td>1852.3</td>
</tr>
<tr>
<td>Cu</td>
<td>Mg</td>
<td>1</td>
<td>1500</td>
<td>934.1</td>
<td>918.3</td>
<td>1852.4</td>
</tr>
<tr>
<td>Fe</td>
<td>Al</td>
<td>6</td>
<td>1740</td>
<td>707.4</td>
<td>702.3</td>
<td>1409.8</td>
</tr>
<tr>
<td>Fe</td>
<td>Mg</td>
<td>1</td>
<td>600</td>
<td>705.0</td>
<td>702.7</td>
<td>1407.7</td>
</tr>
<tr>
<td>Cu</td>
<td>Al</td>
<td>0.8</td>
<td>1200</td>
<td>933.9, 930.4</td>
<td>917.8, 919.3</td>
<td>1851.7, 1849.7</td>
</tr>
</tbody>
</table>

8.9 Future developments

8.9.1 Design improvements

Three further developments for this work have been initially identified as priorities if this technique is to become more widely used, these are:

1. Substrate modification
2. Substrate cooling
3. Increased instrument sensitivity

Substrate modification was investigated by switching from a solid metal substrate to aluminium foil and eventually to a sub-micron thick foil. The use of an even thinner foil <0.8 μm, could be investigated. It is possible to purchase 50 nm thick aluminium foils. However, moving to thinner foils introduces problems in manufacturing and in handling. This would significantly hinder the ability to use the material in a laboratory, unless a suitable substrate could be purchased pre-made ready for particle disposition. Additionally, based upon Phi-Rho-Z simulations the maximum depth of Al Kα emission is 1.8 μm but more than 50% of the x-rays are produced in the first 0.6 μm of aluminium, for primary beam energy of 15 keV. This indicates that a foil stack, with layers ~0.5 μm thick could be even more effective as the x-ray yield would be high while ensuring the number of low energy electrons in the first foil layer are minimised, preventing excessive heating.

An alternative to an aluminium foil stack as a substrate was investigated but could not be tested experimentally during this project because of the high cost involved. This was the use of a thin layer of aluminium deposited onto a diamond surface for use as a substrate. These materials are currently used as high power x-ray anodes. The higher thermal conductivity of the diamond backing, compared to copper enables the anode to be operated at higher powers, as the excess heat is removed by the coolant. For some cost, it would be possible to produce a one off diamond coated with aluminium as an experimental substrate.

Substrate cooling could be investigated by utilising a cold stage, which can circulate a coolant fluid around the stage to cool the entire sample holder, as is routinely carried out using water for x-ray anodes.

A newer instrument could also be utilised for the analysis. This work was undertaken on a MICROLAB 350. In this system the design of the hemispherical analyser, detector array and processing electronics for the
analyser are more than 15 years old. A modern analyser and electronics system is capable of doubling the instrument performance. Modern systems can also be fitted with a magnetic immersion lens such as that in the ESCALAB 250xi, these can triple the count rate by focusing the electrons that are emitted, at all angles, from the sample into the transfer lens of the analyser. An estimation from the instrument manufacturer suggested that a count rate improvement of at least five times would be possible on a new system [130]. This could allow for far more routine analysis of small features as data acquisition times would be drastically reduced and the signal to noise would be improved.

**8.9.2 Future instrument design**

The size of the x-ray excitation and emission envelope far exceeds the size of the electron beam spot at the sample surface. Therefore, a high performance, high spatial resolution, electron gun is unnecessary. Additionally, it was found that the use of small rastered areas instead of point analysis helped ameliorate the thermal degradation of the small particles. Therefore, the high spatial resolution of the electron source used for this work was not needed. The high end Auger field emission gun (FEG) could be replaced with a more common 100 nm FEG or LaB$_6$ electron beam sources which are fitted to many standard laboratory XPS instruments.

Another possible consideration to the analysis of small, surface features is the use of a fine sharp needle that could be brought in close to the feature of interest and used as the x-ray anode. By allowing the electron beam to strike it and not the substrate surface, heating of the substrate should be minimised. A schematic of the possible setup is shown in Figure 8.33. While this procedure might prove cumbersome, needles of a similar size that would be required for this approach are already routinely used inside vacuum systems. They are employed as the manipulators used for lift off/take out of thin foils produced in a focused ion beam microscope.

![Figure 8.33 Schematic for the setup of proximal XPS using a needle anode.](image)

**8.10 Conclusions**

The experimental work in this chapter was undertaken as an initial proof of concept for a new experimental method for the photoelectron analysis of sub-micron particles and features. It has been shown that chemical
state information can be extracted from individual sub-micron particles deposited onto a foil substrate, within a laboratory based instrument.

An interesting result was that an improvement in the signal to noise was observed as the size of the analysed particles decreased. This was thought to be a result of the generated x-rays being able to excite photoelectrons from the entire surface of the smaller particles.

The use of a thin foil substrate was found to improve a problem with particle reduction caused by the localised heating of the substrate by the electron beam. This was also helped by using rastered boxes instead of traditional point analysis for the electron beam.

Trace levels of impurity or alloying elements in the substrate material had a negative impact on the quality of the results obtained, as the Auger peaks generated by them were similar in magnitude to the photoelectron peaks. Therefore this work should only be carried out using the highest purity substrate materials available.

This technique does not require a high end Auger electron gun and instead could be implemented on a laboratory based XPS system fitted with a medium resolution electron gun. This enables the technique to be readily adapted for a standard XPS system, unlike the initial investigations which required dedicated specially designed instruments [125–127]. Additionally, standard samples can be analysed, unlike the specially prepared thin foils required for the original investigations utilising locally excited x-rays.
Chapter 9 - Discussion

9.1 Spectra
At the onset of this project it became apparent that given the specialist applications of beryllium and beryllium compounds there were no modern high quality photoelectron or Auger spectra of beryllium in the literature. Previous Auger investigations have used the technique as a means to track elements without publishing individual spectra or listing the peak energies. Additionally, older studies have also shown Auger spectra in the differential form which is difficult to compare to modern data which is displayed in the direct form.

Therefore, as a starting point for the experimental investigation of beryllium, reference quality spectra were obtained from beryllium and beryllium compounds using XPS and AES. The acquisition of the spectra proved challenging and required significant experimental adaptation. These spectra enabled the chemical states of the compounds to be accurately determined. The Auger spectra from beryllium, beryllium oxide (native and bulk oxide), beryllium nitride and beryllium carbide were obtained and have been published together with the raw data. All of which is now available for other researchers interested in these materials.

This data will enable other researchers to optimise their analysis and ensure the accuracy of their results. In addition to the Auger data, photoelectron spectra were acquired from beryllium metal and bulk beryllium oxide and this data was also published. By combining these data sets with literature values for the photoelectron peaks of the nitride and carbide it was possible to construct the first Wagner chemical state plot for beryllium compounds that contained more than just metallic beryllium. This diagram will enable other researchers to accurately identify the chemical state of beryllium independently of sample charging in photoelectron spectroscopy.

The Auger transitions and the spectral components of beryllium compounds, pose an interesting question for Auger analysis. Beryllium atoms only have four electrons and so the oxide and other beryllium compounds would appear not to have enough electrons to form a $KLL$ Auger transition. However, the oxide, nitride and carbide were all shown to form an Auger transition. These Auger transitions are generated using electrons from the valence band and from spectator states. Spectator states are electrons that originate from the orbitals of the atom bound to beryllium. The energy of the observed transitions within the Auger spectrum can be used to identify the exact electron orbitals involved. Without the extensive investigation of the beryllium compounds it would not be possible to identify these states. This work led to the optimisation of the spectrometers and a fundamental understanding of electron spectroscopy prior to the study of the microstructure of beryllium and subsequent corrosion investigations.

9.2 Microstructure of beryllium
Upon completion of the literature review, it became apparent that a wide range of inclusion compositions with various sizes are present in beryllium. Thus, a detailed investigation of the microstructure of beryllium
was performed, utilising the spectroscopy expertise obtained during the initial work investigating beryllium, to examine and accurately characterise these second phase particles.

The compositions of such particles included: BeO, Al₂O₃, AlFeBe₄, Be₃N₂, Ti₃Si, CdZr, and elemental silicon. Additionally, a range of mixed composition particles were identified which contained nickel, silver and copper as well as other transition metals in trace concentrations. The BeO inclusions are the most numerous type and were dispersed along the grain boundaries throughout the metal as discreet small particles. The presence of these cannot be avoided in beryllium produced by a powder metallurgy route.

The second most common particles were AlFeBe₄ precipitates. These were distributed along grain boundaries and tended to be long and thin because they are formed by precipitation during over aging of the metal, at which point the grain structure is already in place and is difficult to displace by a growing particle. The remaining particle types all tended to be more spherical in geometry compared to the long thin AlFeBe₄ precipitates. Beryllium nitride and intermetallics containing cadmium and zirconium were particularly uncommon. Little evidence was found during the examination of the samples of beryllium carbide inclusions. This was likely to have been a consequence of their rapid hydrolysis in air at which point they would, analytically, resemble oxide inclusions. In addition to the absence of carbide inclusions, no iron beryllide (FeₓBe₀₋ᵧ) type inclusions were identified in the samples of S-65 beryllium.

### 9.3 Corrosion of aluminium

An aluminium alloy specimen was used as an analogue of beryllium to establish safe working practices with a non-toxic material. This was performed in parallel with some of the initial microstructural work identifying the range of second phase particles in beryllium. The use of aluminium proved to be especially helpful in determining that the use of a glovebag to contain beryllium for the corrosion investigation was not suitable. The intricate manipulation of samples required to secure them to holders for analysis was not possible using the fitted gloves. Therefore, the glovebag was replaced with a custom built glovebox. This enabled the safe containment of beryllium and the fine manipulation of samples required for the experimental procedure.

The corrosion of aluminium showed that not all second phase particles were equally active and that corrosion phenomena varied according to the composition of the second phase particle. The higher the copper content the greater the expected potential difference between the particle and the surrounding matrix. This trend was reflected in the corrosion process associated with the three inclusions studied. A copper rich particle showed active accelerated dissolution of the adjacent matrix, with the deposition of corrosion products on the surface of the inclusion. A schematic of the corrosion process involved is shown in Figure 9.1.
The behaviour is explained by the electrochemical potential difference between the particle and the matrix, which is ~600 mV. The Al₆Cu₂Fe particle, being particularly more noble than the surrounding 7075 alloy acts as a local cathode with the adjacent matrix acting as the corresponding anode. Corrosion proceeds through the electrode half reactions shown below. The reactions have been rounded to integer values for clarity.

Anodic reaction:

\[
Al \rightarrow Al^{3+} + 3e^- 
\]

Cathodic reaction:

\[
3O_2 + 6H_2O + 12e^- \rightarrow 12OH^- 
\]

The aluminium cation is attracted to the negatively charged cathode and diffuses to the surface where it reacts with the hydroxyl ions and forms aluminium hydroxide which is precipitated from solution. The zinc and magnesium in the alloy that are also dissolved will also form part of these precipitated corrosion products, as shown below:

\[
Al^{3+} + 3OH^- \rightarrow Al(OH)_3 \downarrow 
\]

\[
Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \downarrow 
\]

\[
Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2 \downarrow 
\]

An intermetallic that contained an intermediate concentration of copper and some iron showed slight dissolution of the matrix, with little deposition of corrosion products on the surface of the particle in addition to crevice corrosion at the matrix/particle interface. An iron-rich, copper-poor intermetallic did not show accelerated corrosion of the matrix but significant crevice corrosion was observed at the matrix interface, a schematic of this corrosion process is shown in Figure 9.2.
The corrosion process is the result of the formation of a differential aeration cell also known as a concentration cell. If electrolyte is present in a crevice between the matrix and a second phase particle, localised attack, in the form of crevice corrosion can occur. Oxygen within the electrolyte in the crevice is consumed via the formation of aluminium oxide and oxychlorides within the crevice. This oxygen cannot easily be replaced by fresh oxygen from the bulk electrolyte as diffusion is retarded by the narrow crevice mouth. At the crevice mouth, oxygen is readily available as diffusion is rapid in the electrolyte. The different oxygen concentrations result in local cell with anodic attack in the oxygen-depleted zone and the disposition of corrosion products at the oxygen-rich cathode near the crevice mouth. The heterogeneity between the particle and the matrix may provide enough of a gap to allow electrolyte stagnation and the initiation of crevice corrosion at the interface.

9.3 Corrosion of beryllium

Corrosion studies in sodium chloride solution, under normal conditions, at the open circuit potential allows the corrosion of beryllium to be studied in a manner that is more representative of the conditions to which beryllium is exposed to and is more relevant to industry. Although the experiment and data acquisition utilised in this thesis requires days compared to the seconds taken to collect electrochemical data the results illustrate the initial processes occurring at the surface of beryllium that lead to localised corrosion.

The random distribution of the inclusions in the beryllium matrix required an alternative methodology that utilised for the aluminium, in order to effectively map the sample surface and enable the reliable relocation of the same second phase particles in the same orientation after each corrosion step. To achieve this, a 26 x 21 grid of microhardness indents were hand pressed into the beryllium surface. Positions of inclusions could then be referenced to a specific grid position. The manual characterisation of all of the particles within this grid would have be prohibitively time consuming and so an automated analysis routine was utilised. The routine calculated the size and recorded the composition of ~2000 second phase particles within the grid. The largest inclusions with compositions of interest were selected.
A total of nine second phase particles were studied with different compositions to assess their role in the corrosion process. It was found that not all of the inclusions led to localised corrosion or had any corrosive activity associated with their presence in the metal surface. The inactive particles included two AlFeBe₄ precipitates, an elemental silicon inclusion and a mixed phase silicon and AlFeBe₄ particle.

The second phase particles identified to have an active role in the corrosion process of beryllium were Al₂O₃, AlFeBe₄ and Ti₃Si particles. The alumina particles, which are actually a mix of alumina and silica, undergo a crevice corrosion processes as depicted in Figure 9.3. The highly insulating particles cannot form a galvanic couple with the beryllium matrix like the intermetallic particles and so do not act as anode or cathodes to the beryllium. However, the crack that is present between the beryllium matrix and the surface of the inclusions provides an ideal place for the formation of a differential aeration cell.

Electrolyte enters the crack by capillary action when the sample is exposed the test solution. The solution effectively becomes trapped in the crack and an oxygen concentration gradient is established between the tip of the crack and the surface. The crack is oxygen poor as diffusion to the surface is hindered by the narrow mouth of the crack. The surface is comparatively oxygen rich as it is always available from the electrolyte. A small potential difference is generated with the anode at the crack tip and the cathode at the oxygen rich surface.

![Figure 9.3 schematic of the processes involved in crevice corrosion at the interface between ceramic inclusions and the beryllium matrix.](image)

The matrix within the crack is dissolved generating beryllium cations, these diffuse to the cathode at the metal surface which produces hydroxyl ions via the reduction of water. The beryllium ions react with the hydroxyl ions forming beryllium hydroxide and the forming pit mouth. The schematic reflects the process observed in Chapter 6, no beryllium hydroxide is depicted on the alumina particle as no beryllium hydroxide
deposits were observed on the alumina surface. The absence of deposited material is again linked to the particle acting as a crevice former. It is an insulator and so cannot support any of the current required for the reduction of water to hydroxyl ions.

The AlFeBe$_4$ and Ti$_3$Si/Be$_2$Ti$_3$Si intermetallics showed highly similar corrosion process. These particles are thought to be anodic to the surrounding beryllium matrix. A schematic of the corrosion process is shown in Figure 9.4. It is believed that the intermetallics undergo dealloying of the most anodic constituent, the beryllium. The particles slightly anodically polarise the surrounding alloy resulting in a circle around the particles that is free from precipitated beryllium hydroxide corrosion products. The anodic reaction at the intermetallic is shown below:

$$Be \rightarrow Be^{2+} + 2e^-$$

This results in a matrix around this region acting as the cathode producing hydroxyl ions. This cathodic reaction in the ring around the particle and polarised matrix is shown below:

$$3O_2 + 6H_2O + 12e^- \rightarrow 12OH^-$$

The beryllium cation is attracted to the negatively charged cathode and diffuses from the surface of the intermetallic to the ring around where it reacts with the hydroxyl ions and forms beryllium hydroxide which is precipitated from solution, as shown below:

$$Be^{2+} + 2OH^- \rightarrow Be(OH)_2 \downarrow$$

The amount of precipitated beryllium hydroxide gradually increases to the point where a dome is formed that covers the intermetallic and a large region of surrounding matrix. For example, the dome that surrounded intermetallic #7 was ~15 μm in diameter, whilst the intermetallic was only 2 μm in diameter. These domes are likely to consist of an inner beryllium oxide shell with an outer hydroxide structure. This has been observed in magnesium/aluminium alloys [131]. The formation of these corrosion product domes has been observed in aluminium alloys on cathodic intermetallics [132]. However, for these particles the dome is much more closely isolated to the particle and matches the diameter of the particle.

An additional process that was observed to occur was the deposition of copper onto the surface of these intermetallics. The source of this copper is likely to be the metal or the corrosive solution. An interesting effect of this copper deposition and dealloying of beryllium is the accompanying change in the potential of the intermetallics with respect to the matrix. The loss of beryllium and deposition of copper would result in a fairly noble particle which would then accelerate the corrosion of material at the interface of the particle and the matrix, as was observed for the copper rich intermetallic in the aluminium investigation. If the corrosion study was extended further this behaviour might eventually be observed. This process of copper deposition onto anodic intermetallics is observed in aluminium alloys for the S phase particles. The aluminium being the most anodic particle constituent, dealloys from the particle forming a ring of corrosion products. The ring eventually evolves into a dome of chlorinated aluminium hydroxide. These domes eventually collapse and the remaining particle switches to cathodic behaviour as it is now rich in manganese and coated with a layer
of copper. This behaviour in aluminium alloy is in agreement with the corrosion processes observed in this thesis for the anodic intermetallics.

The identification of these active inclusions raises the question if these could be removed from beryllium to improve the corrosion resistance of the metal. The AlFeBe₂ precipitates are required within the metal to remove free aluminium which adversely effects ductility. Additionally, they remove iron beryllides which have an undesirable effect on the corrosion performance of beryllium in neutral halide solutions.

The alumina particles which led to significant crevice corrosion were most likely present as impurities particles in the beryllium feedstock powder. These would have been introduced from the ceramic ball milling media used to produce the beryllium powder. All milling media undergoes wear, losing material as it mills. Therefore, it would be difficult to avoid these as the smallest grain sized and isotropic metal is produced from ball milled powder.

Based upon the observations made during the experimental work and the corrosion processes associated with the second phase particles that were studied it is possible to predict the corrosion process that might occur with particle compositions that were not studied. It is thought beryllium oxide inclusions, if they are large
enough, would result in the same form of crevice corrosion as observed for the ceramic inclusions. This is because the oxide being a good insulator would not be able to form a galvanic couple with the metal matrix but does provide a site where a crack might form.

Another inclusion type that was not studied was beryllium carbide particles. It is thought that one of the particles may contain some subsurface carbide but this could not be confirmed. These particles should undergo hydrolysis instead of forming a galvanic couple with the beryllium. As such they should behave in the same manner as a highly anodic particle, with the dissolution of the particle to leave a pit.

9.4 Proximal XPS

Proximal XPS could be used to probe the chemistry of corrosion products associated with the active second particles and possibly confirm that they are beryllium hydroxide. The reasons why this would not be possible using beryllium metal as the x-ray source were previously discussed in Chapter 8, however, aluminium does make a suitable x-ray source material. Corrosion product deposition was observed at the crevice surrounding alumina particles in the metal matrix. It might be possible to use the aluminium in the aluminium oxide inclusions as a local x-ray source to excite photoelectrons from these corrosion products. The use of aluminium oxide x-rays would require a slight adjustment to the x-ray photon energy to ensure the binding energies were correct following the acquisition of photoelectron spectra.

In the same manner, the aluminium present in the AlFeBe₄ precipitates could also be used to probe the chemistry of the local environment. Additionally, the environment surrounding the Ti₃Si inclusions could also be probed using silicon x-rays. The adjustments required for the Al Kα and Si Kα photon energies could be obtained by performing high resolution WDX on the inclusions to determine the exact energy of the emitted x-rays.

For large inclusions, where the x-rays are fully attenuated within the inclusion, the x-rays from the particle could be used to probe the chemistry of the surface oxide. Reducing the beam potential would minimise the risk of secondary x-ray fluorescence from the particle exciting material from the matrix, which would affect the results from the particle surface. Chemical assessment of the oxide may reveal information to help ascertain why certain particles cause pitting corrosion while others of the same composition and size do not.

The technique has the potential to have a huge impact in the analysis of small particles. The Phi-Rho-Z simulations in Chapter 8 showed how the region of excitation was maximised for a copper particle of <300 nm in size as the aluminium x-rays were fully attenuated within this depth of material. Repeated simulations using organic particles show this depth of material to be ~3 μm. Additionally, transition metal particles showed similar results to the copper particle, the x-rays are attenuated within ~500 nm of material. As such, maximum photoelectron excitation would be expected from particles of this size and smaller. This represents an excellent size range for probing the surface chemistry of small particles. With further development it may eventually become possible to study the chemistry of organic coatings on individual sub-micron particles.


9.5 Chlorinated solvents

Beryllium was found to undergo localised corrosion in sodium chloride solution but is known to be remain corrosion free in pure water for many years. The metal in this case must be free from contamination that can introduce corrosion precursors into the environment in which it is used or stored. As such, the use of six chlorinated solvents for the vapour degreasing of beryllium were investigated, as their use had been associated with surface chloride formation. They represented a selection of solvents that had previously been thermodynamically investigated for compatibility with beryllium. The experimental setup replicated the vapour degreasing process that metal components typically undergo. Despite the modelling predicting no chloride formation for three of the solvents, all of the solvents produced the beryllium chloride, in addition to adsorbed solvent resulting in organic chlorine also being present at the surface.

The behaviour of the six traditional solvents was compared to drop-in replacement cleaning solvents. These produced no detectable chloride formation or solvent residue. With the careful selection of solvent stabilisers and metal inhibitors the use of traditional solvents could be continued. However, the use of the drop-in replacements has additional advantages such as: being non-flammable, non-ozone depleting non-toxic and leaving a reduced amount of solvent residue at the surface. As such, they are gradually replacing the older solvents.

Three beryllium samples were submerged in water for 30 days and the presence of chloride at the metal surface did appear to accelerate the rate of corrosion of beryllium whilst organic chlorine, from a solidified film of insoluble pentachlorobenzene, did not appear to affect the rate of corrosion. The solidified film may have acted as a passivating coating by preventing contact between the metal surface and the electrolyte.

The vapour degreasing process is essential to producing a clean finished metal surface. The use of traditional chlorinated cleaning solvents does lead to the formation of the metal chloride corrosion precursor. However, since the general phasing out of these solvents in favour of modern formulations, with proprietary inhibitors and solvent stabilisers, the risk to the surface integrity appears to have been minimised even without the addition of a rinsing step.

The apparent general corrosion of beryllium observed in chlorinated solvents has been shown to, on the whole, be related to thermodynamic principles.

In order to study the corrosion phenomena associated with S-65 beryllium the work has shown the importance of: high quality reference spectra, a thorough appreciation of the material microstructure, the requirement for a non-toxic corrosion analogue and requirement to investigate a wide range of particle compositions.
Chapter 10 - Conclusions and Further Work

10.1 Conclusions

In this thesis a corrosion study was conducted on AA7075-T6 as a learning tool for the safe handling of a non-toxic material and to understand the techniques available for the analysis of second phase particles. Following this, an electron and x-ray spectroscopic investigation of beryllium was performed in order to obtain high quality spectra from beryllium, enabling the identification of the chemical states of beryllium. Second phase particles were also examined to further understand their size and composition. A corrosion study was then conducted on S-65 beryllium as the primary material of interest. A range of particle compositions were selected which represented the most common particle types. These were examined following successive immersion, in NaCl solution, to establish their role in the corrosion process. The effect of vapour degreasing beryllium using chlorinated solvents was also investigated to study the solvents compatibility with beryllium and investigate the formation of corrosion precursors on the metal surface. In addition to these investigations, a proof of concept work for a novel surface analysis technique enabling chemical state information to be extracted from micrometre scale particles and features was also undertaken.

The work in this thesis led to the following conclusions:

- High quality Auger spectra can be collected from highly insulating bulk beryllium oxide and beryllium carbide using the correct experimental procedure.
- The energy of the modified Auger parameter for beryllium, beryllium nitride, beryllium oxide and beryllium carbide have been calculated, enabling the construction of a Wagner chemical state plot for beryllium.
- Combining low primary beam energies with WDX allows the unambiguous confirmation of beryllium in intermetallics.
- The majority of the second phase particles identified in S-65 beryllium billet were BeO, Al₂O₃, elemental silicon, Ti₃Si and AlFeBe₄.
- These particles were often heterogeneous. The large Al₂O₃ inclusions were observed to have AlFeBe₄ and silicon phases present are their edges. Elemental silicon particles were often found with AlFeBe₄ precipitated onto them.
- The Al₂O₃ inclusions were the largest, often reaching sizes of up to 50 μm. The inclusions with all other compositions were rarely larger than 5 μm.
- Second phase particles could be reliably relocated in the same geometry and position after many corrosion steps enabling true time lapse analysis using SEM, EDX and AES.
- Of the particles studied the compositions: AlFeBe₄, Ti₃Si and Al₂O₃ were found to act as corrosion initiation sites.
- The AlFeBe₄ and Ti₃Si intermetallics were found to be anodic with respect to the matrix, with the apparent dissolution of beryllium and the formation of domes of corrosion products.
• Copper deposited onto the surface of the AlFeBe₄ and Ti₃Si intermetallics which is likely to change their properties in later corrosion stages.
• A previously unobserved corrosion process was found to occur at the site of the Al₂O₃ particles present in beryllium. These inclusions provided a unique site for the development of crevice corrosion in the crack formed between the interface of the metal and the ceramic inclusions, resulting in dissolution of the surrounding subsurface matrix.
• The use of chlorinated solvents for vapour degreasing showed that selecting a suitable combined with a final rinsing stage after degreasing minimises the amount of inorganic chloride on beryllium.
• Extraction of chemical state information from individual sub-micron particles using a novel surface analysis technique is possible and further work in this area may show the technique to be successful in the analysis of small surface features.

Finally, the original contributions to knowledge in this thesis include:

1. The development of an understanding of the microchemistry associated with three intermetallic phases present in AA7075-T6.
2. The establishment of high quality reference spectra for beryllium and beryllium compounds.
3. The production of a chemical state Wagner plot enabling chemical state information to be extracted from beryllium compounds independently of sample charging in photoelectron spectroscopy.
4. Developed the understanding of the behaviour of important second phase particles in beryllium and their role in the localised corrosion of beryllium.
5. An expanded range of chlorinated solvents have been tested for compatibility with beryllium.
6. Shown that the inorganic chloride formed on a beryllium surface following vapour degreasing accelerates corrosion while the organic chlorine does not.
7. Developed a new experimental methodology that enabled the acquisition of chemical state information from the surface of sub-micron features.

10.2 Future work

Further to the investigation carried out in this thesis the work could be expanded by investigating the electrochemical potential of the individual second phase particles found to be involved in the corrosion of beryllium. This could be performed using scanning Kelvin probe force microscopy (SKPFM). The particles could be analysed using the same techniques used in this thesis with the addition of SKPFM performed before and after each corrosion step. This technique has been widely improved to investigate the corrosion processes of aluminium alloys and has revealed new information that was unobtainable using traditional characterisation techniques [92,133]. This work would lead to an enhanced understanding of the driving force in the corrosion of beryllium and provide additional data for the corrosion model being built by AWE.

During this project a day of SKPFM was undertaken as a proof of concept for this work on a polished beryllium sample. A number of large intermetallics were identified within the microhardness indent grid which had previously been analysed using EDX to ensure their composition was known. Figure 10.1 shows
the SEM micrograph of the indent grid and the SKPFM potential map from the region highlighted in the SEM micrograph. The potential map was rotated anticlockwise by 90° to align with the SEM FOV. The large second phase particles are observed in the map as dark patches. A number of much smaller intermetallics are also observed within the field of view.

![Image of SEM micrograph and SKPFM potential map](image)

**Figure 10.1** SEM micrograph and a SKPFM potential map of the beryllium surface over a 40 μm area. Two large intermetallics are located within the frame.

EDX of the particles showed them to be Al$_2$O$_3$ (blue arrow) and Ti$_3$Si (white arrow). Line profiles were extracted from each of the maps that bisected each of the inclusions. These profiles are shown in Figure 10.2. Negative potentials for each of the intermetallics were measured. These were -400 mV and -660 mV with respect to the beryllium for Ti$_3$Si and Al$_2$O$_3$ respectively. These values indicated anodic activity, which was found for the Ti$_3$Si intermetallics but not for the Al$_2$O$_3$ inclusions. The negative value for the alumina particle was likely to have been a consequence of it being an insulator.

![Image of line profile through two intermetallics](image)

**Figure 10.2** Line profile through the two intermetallics from the SKPFM potential map.

The instrument was not previously calibrated using the aluminium on gold standard required for SKPM analysis and so these values should not be taken as absolute, merely as evidence that the technique could prove highly useful for furthering the understanding of the beryllium corrosion processes.
Further work into the compatibility and the effect of various solvents on the surface of beryllium is planned. These solvents were designed as drop-in replacements for chlorinated solvents, which have generally been phased out in recent years. The solvents will be selected from a range of commercially available cleaning solutions which will be important in understanding the potential risks of corrosion precursor formation on beryllium in the future. This work is planned for Spring/Summer as another MEng project.

A wider reaching section of work that would be undertaken by the industries that manufacture and use beryllium would be to lessen the propensity of S-65 beryllium to corrode by reducing the number of active second phase particles present in the metal.
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