CHARACTERISATION OF Ti-6Al-4V/GLASS-CERAMIC AND PRE-OXIDISED KOVAR/GLASS-CERAMIC INTERFACES

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Abstract

Glass-to-metal seals are used in a wide range of components. The nature of the interfaces between the constituents is often crucial to the performance of the seal and thus the aim of this study was to characterise the various interfaces in a novel seal made from a strontium boroaluminate glass-ceramic and the alloys Ti-6Al-4V and Kovar (Fe-29Ni-17Co). A titanium boride was found, by STEM, EELS and WDX, to have formed at the glass-ceramic to Ti-6Al-4V interface and to be bonded to both the metal on one side and the glass-ceramic on the other, in contrast to the classic view of glass to metal interfaces where bonding is thought to be promoted through metal dissolving into the glass / glass-ceramic. To establish bonding at the other interface, it was necessary to grow an oxide layer on the Kovar, by heating in air at 700 °C or 800 °C for 10 minutes. The oxide grown at both temperatures was shown (by XPS, XRD, SEM, EDX, STEM and Raman) to have the same composition, with the only significant difference being thickness \((2.1 \pm 0.6) \mu m\) and \((4.0 \pm 0.2) \mu m\) thick, for the oxides grown at 700 °C and 800 °C respectively. However, the oxide was found to be much more complex than was indicated by prior literature, comprising four layers. The top layer of the oxide was \((Fe, Co)_3O_4\), with an \(Fe_2O_3\) layer beneath it. Below these layers were a further two layers of \((Fe, Co, Ni)_3O_4\). When heated to 800 °C, to simulate the sealing conditions, the oxide was changed to an \(Fe_3O_4\) layer with metallic cobalt and nickel inclusions. Bonding was shown, by SEM and STEM, to occur between the oxidised Kovar and the glass-ceramic, as a result of dissolution of iron from the oxide into the glass. Although the interfaces were not definitively optimised, the seals produced were satisfactory and hermetic.
Acknowledgements

I would like to thank my supervisors Dr Mark Whiting and Prof. Julie Yeomans for guiding me through my time working on my Ph.D. and everyone else in the department who has offered help and advice along the way. Dr Chris Mallinson was a massive help throughout, and especially during the write up. Martyn Staff deserves a special mention for refining and producing the seals, which were essential for the work. Thanks to Sabrina for help, support and encouraging me to sit and write! And all of my friends, but especially Joe and Jonny who were fantastic for the whole of my Ph.D. Thanks are also due to the EPSRC and the University of Surrey for my funding, and finally coffee, without which I could never have written a word!
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Abbreviations

CTE  Coefficient of thermal expansion
EDX  Energy dispersive x-ray spectroscopy
EELS Electron energy loss spectroscopy
FIB  Focussed ion beam
SEM  Scanning electron microscope
SRBAL Strontium aluminoborate glass / glass-ceramic
STEM Scanning transmission electron microscope
WDX  Wavelength dispersive x-ray spectroscopy
XPS  X-ray photoelectron spectroscopy
XRD  X-ray diffraction
Chapter 1

Introduction

1.1 Project context and aims

Glass-to-metal seals are used in a wide variety of components, typically where electrical connections are needed through metal components (for example passing wire into and out of a pacemaker). Glass-to-metal seals are also important when components need to be sealed and able to withstand high temperatures and pressures, such as in oil and gas rigs. Good seals need to have some degree of strength and mechanical integrity and usually need to be hermetic (leak tight). The degree to which the different qualities are required varies with the intended use. Glass-to-metal seals typically have a circular geometry, to avoid stress concentrations, with a central metal wire or pin. It is the pin that is integrated into the electrical circuit of which the seal is a part.

Seals can be made reliably and with good properties using combinations of stainless steel and silicate glasses / glass-ceramics. There is a significant body of work in this area. However, new applications and requirements mean that other materials are being considered. Titanium is an interesting candidate for glass-to-metal
sealing because of its high specific strength and thus the ability to make lighter components than is the case with steel. Titanium is also preferred in biomedical applications, some of which require glass-to-metal seals. In many demanding applications it is also a requirement that the seals should be stable and continue to be hermetic for prolonged periods of time. In the case of titanium glass-to-metal seals it has been shown that seals can be made with borate glasses, whereas using silicate glasses with titanium is generally unsuccessful. There is not, however, an extensive body of work on titanium to borate glass-to-metal seals and in particular there is a lack of information pertaining to the interface in these materials even though these are crucial to seal performance. Thus, the primary aim of this research is to determine the nature of the interfaces.

The work presented here forms a part of a larger project investigating the use of titanium for seal components. Some preliminary work had been carried out prior to this study commencing but much of the development was undertaken in parallel with the work presented here. Specifically, the materials to be used in the seal were already selected. Having identified Ti-6Al-4V as the material of choice for the housing, the borate glass compositions were narrowed down using the following criteria. Firstly, the melting temperature had to be above 500 °C, so that the final component could be expected to withstand similar temperatures, but below 900 °C so that it was below the allotropic phase transition temperature of the titanium alloy used. Additionally the coefficient of thermal expansion had to be equal to or lower than that of titanium so that a matched or compressive seal could be formed. Finally, the temperature difference between the glass transition temperature \( T_g \) and and crystallisation temperature \( T_x \) was chosen to be greater than 150 °C, to prevent unwanted crystallisation during

\(^1\)where titanium is referred to in relation to any work performed as a part of this project, it is the titanium alloy Ti-6Al-4V that is meant
1.1. Project context and aims

The pin materials were then chosen so that the coefficient of thermal expansion was suitable for the specific glass used. A few iron-nickel alloys were considered for the pin material at the beginning of the project because of their good electrical properties and suitable coefficients of thermal expansion (i.e. below that of titanium) but only Kovar was successfully used to produce a hermetic seal. Hermetic seals were only possible when the Kovar had been oxidised to produce a surface oxide layer a few micrometers thick.

The choice of processing conditions is important in any glass-to-metal seal and a range of heat treatments were trialled in the first half of the project. Through trial, error, and iteration a heat treatment that resulted in seals that did not crack and were hermetic was found and then used for the remainder of the project. The bulk properties of the materials, while important for seal manufacture, were not the focus of the work and were performed, to the degree necessary, by others working in parallel on the broader project. The main aim of this project was to characterise the interfaces between the glass (or glass-ceramic) and the metals in the seals.

Thus, the objectives of the work were at the outset of the project:

1. characterise the reactions that occur between titanium and the boroaluminate glass-ceramic during sealing

2. identify the oxide that forms on Kovar pins when oxidised in air

3. characterise the reactions that occur between Kovar and the boroaluminate glass-ceramic during sealing

4. draw conclusions regarding the nature of the bonding, to assist in forming satisfactory glass-to-metal seals in this system as well as other systems
1.2 Outline of thesis

After this introductory chapter, an overview of glass-to-metal sealing is given, discussing the different types of seal, bonding models, and factors to be considered in sealing. The materials used in the seals are discussed (Ti-6Al-4V, Kovar and boroaluminate glasses / glass-ceramics) and the existing work dealing with the joining of Kovar to glass and titanium to boroaluminate glasses is reviewed. From this it is clear that there is a need to study further the interfaces of the titanium and boroaluminate glass seals and, as such, this is examined further in Chapter 4. Consideration of the literature on the oxidation of Kovar shows that there is not a clear consensus and therefore the oxide layers grown on the samples used for seal production in this work are studied in Chapter 5. This is followed by a study of the bonding between the oxidised Kovar and boroaluminate glass-ceramic. Finally there is a discussion of the bonding model used in glass-to-metal sealing with reference to the interfaces studied, followed by conclusions and some suggestions for further work.
Chapter 2

Literature Review

2.1 Introduction to glass-to-metal sealing

2.1.1 Introduction

Two monographs have been published by the Society of Glass Technology, the first written by Partridge in 1949 [76] and a more recent publication by Donald in 2009 [25]. Both provide excellent detailed summaries of many areas of glass and glass-ceramic-to-metal sealing ranging from historical background to practical advice and theoretical background and covering a broad range of techniques, metals and glass compositions.

This chapter gives an overview of the main types of glass-to-metal seals followed by a discussion of the theories of bonding in glass-to-metal seals, the importance of wetting and the effects of stresses in seals. The materials used in the seals, Ti-6Al-4V, Kovar (Fe-29Ni-17Co) and boroaluminate glasses, are discussed. Practical results from sealing titanium alloys to glass are given next, and then sealing
glasses to Kovar is covered. Finally the oxidation of Kovar is discussed, since it is important that it is oxidised before being sealed to glass.

### 2.1.2 Types of seal

Glass has a number of properties that lend it to use in seals for electronic components requiring sealing, namely that it is a good insulator, reasonably impervious to gases, mechanically stable, can be processed easily and can be bonded strongly and hermetically to metals. However, there are some issues to be addressed. One of the major problems faced when designing a glass-to-metal seal is the difference between the coefficient of thermal expansion (CTE) of the glass and that of the metal. Since the seal must be made at a temperature high enough for the glass to flow there can be significant volume changes on cooling which create stresses within the joint. Additionally, reactions between the glass and metal can create products that change stress states around the interfaces. Glasses are relatively weak in tension and as such if a seal fails due to excessive stress the failure usually occurs within the glass.

Early glass-to-metal sealing developed from the incandescent light bulb industry and was extended to allow the production of many electrical components such as vacuum tubes, reed switches, and microelectronic packaging [25]. The early seals relied on using ductile metals that could deform to reduce the heating-induced stresses in the glass at the join. This is similar to a houskeeper seal, an early type of glass to metal seal where a copper (or other ductile metal) tube can be joined to a glass tube. The copper is thinned to a sharp point so that the stresses in the glass are reduced since the copper can be deformed easily [39]. This method allows even very large components to be joined without deleterious effects due to the CTE mismatch.
2.1. Introduction to glass-to-metal sealing

Subsequently, other methods have been developed and a number of sealing glasses have been developed for a range of different metals [76, 25]. A few varieties of the sealing glasses that are commercially available are shown in Table 2.1 and some experimental sealing glass compositions are shown in Table 2.2.

Table 2.1: A small selection of the commercially available sealing glasses, intended to give an idea of the range available, (as given by Donald [25]).

<table>
<thead>
<tr>
<th>Glass</th>
<th>Type</th>
<th>Softening temp. / °C</th>
<th>Working temp. / °C</th>
<th>CTE x 10⁻⁶ °C⁻¹</th>
<th>Temp. range / °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morgan</td>
<td>high expansion</td>
<td>-</td>
<td>-</td>
<td>13</td>
<td>0-300</td>
</tr>
<tr>
<td>GBC226</td>
<td>Pb-free</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Schott</td>
<td>FeO containing</td>
<td>708</td>
<td>1035</td>
<td>9</td>
<td>2-300</td>
</tr>
<tr>
<td>8512</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GB Glass</td>
<td>alkaline earth</td>
<td>720</td>
<td>-</td>
<td>7.5</td>
<td>50-400</td>
</tr>
<tr>
<td>GS77</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Corning</td>
<td>borosilicate</td>
<td>718</td>
<td>980</td>
<td>5.1</td>
<td>0-300</td>
</tr>
<tr>
<td>7056</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Corning</td>
<td>borosilicate</td>
<td>712</td>
<td>1128</td>
<td>4.6</td>
<td>0-300</td>
</tr>
<tr>
<td>7052</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Morgan</td>
<td>borosilicate</td>
<td>820</td>
<td>-</td>
<td>3.2</td>
<td>0-300</td>
</tr>
<tr>
<td>GBC510</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.2: A small selection of experimental glass compositions, intended to give an idea of the range studied, (as given by Donald [25]).

<table>
<thead>
<tr>
<th>Glass</th>
<th>Type</th>
<th>Softening temp. °C</th>
<th>CTE x 10⁻⁶ °C⁻¹</th>
<th>Temp. range °C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>S2</td>
<td>silicate glass</td>
<td>500</td>
<td>11.9</td>
<td>20-400</td>
<td>McMillan, Partridge &amp; Ward, 1979</td>
</tr>
<tr>
<td>BS1</td>
<td>borosilicate glass</td>
<td>435</td>
<td>14.4</td>
<td>20-400</td>
<td>McMillan, Partridge &amp; Ward, 1979</td>
</tr>
<tr>
<td>BS7</td>
<td>borosilicate glass</td>
<td>460</td>
<td>5.4</td>
<td>25-460</td>
<td>Dalton, 1946</td>
</tr>
<tr>
<td>P1</td>
<td>phosphate glass</td>
<td>212</td>
<td>34.7</td>
<td>100-250</td>
<td>Peng &amp; Day, 1991</td>
</tr>
<tr>
<td>P14</td>
<td>phosphate glass</td>
<td>330</td>
<td>11.6</td>
<td>100-200</td>
<td>Ashara &amp; Izumi-tani, 1975</td>
</tr>
<tr>
<td>LZR2</td>
<td>lead zinc borate glass</td>
<td>334</td>
<td>11.7</td>
<td>50-250</td>
<td>Ishiyama, 1996</td>
</tr>
<tr>
<td>V1</td>
<td>vanadate glass</td>
<td>328</td>
<td>11.8</td>
<td>25-150</td>
<td>Malmendier &amp; Sojka, 1975</td>
</tr>
</tbody>
</table>
Selecting the components to have particular thermal expansions gives different categories of seal, matched and compressive. In a matched seal the coefficients of thermal expansion of the glass and metal are matched, as the name suggests. In a compressive seal the CTEs are chosen such that the majority of the glass is in radial compression, since glass is stronger in compression than tension whilst the metal is usually ductile enough to withstand some tensile stress without cracking. This requires the glass to be surrounded by the metal. Compressive seals have higher strength and are often hermetic simply as a consequence of the tight fit created by the components shrinking down together [25]. A circular design is typically used to distribute stresses symmetrically, illustrated schematically in Figure 2.1. One can also place pins of another metal with lower CTE than the glass down the centre of the glass so that each of the components shrinks down onto the next. Matched and compressive seals are the most common, though others such as unmatched and soldered seals are also used.

![Figure 2.1: Schematic diagram of a typical cylindrical seal geometry.](image)

### 2.1.3 Bonding theories

Several theories and approaches have been proposed to explain the bonding of glasses and glass-ceramics to metals. It is now accepted that chemical bonding
is the dominant mechanism for bonding [25], though there is also a contribution, of varying importance, from mechanical keying.

Early observations of glass-to-metal seals and coatings noted that the interface was often rougher once joined than the surfaces were before the two had been joined. Two theories were proposed, (i) that metal dendrites grew into the glass and allowed mechanical keying [48, 34], (ii) that galvanic corrosion of the metal created pits that could key the substrates together [70, 99]. However, the theories fell out of favour because the ease of reduction of one substrate by the other does not correlate with the strength of the bond (although much of the interface roughness is developed during firing) [87]. It is still the case that roughness correlates with adherence but it is not generated through reactions at the interface, rather it is due to factors such as increased mechanical keying and increased contact area.

According to the chemical bonding theory proposed by Pask in 1987, bonding occurs when the glass can be, and remain, saturated by the oxide of the metal to be bonded [78]. This allows a region to be formed where there is a transition from the metallic bonding in the metal to the ionic or covalent bonding in the glass. Pask states that the strongest bonding is achieved when a monoxide layer is formed since if there is a defined region of metal oxide at the glass-metal interface the bond strength is limited by the adherence of the metal oxide to the bulk metal. With a metal oxide saturated region in the glass, a metal-metal bond can exist between the metals atoms in the bulk metal and the metal ions in the glass [47]. This bonding is much stronger than if there is no oxide layer present. Without an oxide layer the bonding is by van der Waals forces and there is not continuous electronic bonding across the interface [78]. Schematic diagrams of these scenarios are shown in Figure 2.2.
The oxide layer can either result from using metal with an oxide layer in place before the sealing or can be created by redox reactions during sealing [25, 78]. Oxidised metal parts were used in practical seal making before the mechanism was understood, with recommendations for pre-oxidation treatments given for different metals [76]. If pre-oxidation is used, the sealing cycle must be chosen such that the oxide layer has been thinned greatly but not dissolved entirely; ideally it would be a single atomic layer of oxide. It is, however, rare to thin the oxide layer to such an extent, since the oxides in the glass may oxidise the metal and maintain an oxide layer despite metal oxides diffusing away from the interface. For example, Jach et al. [42] studied a pure iron - sodium disilicate glass system in air and observed that the interfacial layer was always thick. Conversely, Pask and Fulrath [79] observed that a disilicate glass on an oxide free iron substrate, in vacuum, did not cause oxidation of the iron (and also did not bond).

Figure 2.2: Schematic diagram of the varying thicknesses of oxide layers that may be present at the glass-metal interface, a thick oxide layer, a monoxide layer or no layer. An adaptation of Fig 4. [78]
The metal oxide concentration in the glass though must not be too great or the CTE may be altered significantly, causing stresses and subsequent seal failure. It should, however, be noted that CTE changes may also be favourable as they can create graded CTE variations across the interface and thus reduce stresses [65, 78, 122].

2.1.4 Wetting

Introduction and theory

It is important to have good contact between the molten glass and metal. This requires the glass to wet the metal since if the glass does not spread across the metal the contact area will be significantly reduced, pits and grooves in the metal may not be filled with glass and pores may exist at the interface. This weakens the bond and reduces the potential for an hermetic seal.

There are many ways to assess wettability, [98], but common methods are sessile drop experiments (which themselves have various techniques) or thermodynamic calculations using the surface free energy of the surfaces involved. Without a high enough degree of wetting, insufficient chemical bonding across the glass-metal interface will be achieved and high seal hermeticity and strength will not be obtained.

Thermodynamically, the liquid glass will spread on the solid metal if the surface free energy of the system is reduced by doing so. However, since the lowest surface area per unit volume of liquid will be achieved by a sphere, there is resistance to spreading. The balance between the various energies is given by Equation 2.1, Young’s equation [121]:
Chapter 2. Literature Review

\[ \gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \] (2.1)

where \( \gamma_{SV}, \gamma_{SL} \) and \( \gamma_{LV} \) are the interfacial energies between the solid and vapour; solid and liquid; and liquid and vapour respectively and \( \theta \) is the contact angle, as shown in Figure 2.3 Young’s equation can be extended to give Equation 2.2, the Young-Dupre equation:

\[ W_A = \gamma_{LV}(1 + \cos \theta) \] (2.2)

by including a term for the work of adhesion \( W_A \), shown in Equation 2.3:

\[ W_A = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \] (2.3)

This is suitable as a first indication of whether conditions may be favourable for wetting but is not a guide to predicting bond strength since it does not account for the effect that a change in the surface may have on the chemical bond strength. This can be accounted for using Equation 2.4 (Loehman, 1988):

\[ W_A = \gamma_{LV}(1 + \cos \theta) + \gamma_{RI} - C\Delta G^o \] (2.4)

where \( \gamma_{RI} \) is the interfacial energy between the solid and the reaction layer, \( \Delta G \) is the Gibbs free energy of the reaction layer, \( C \) is a constant.

Factors affecting wetting

The precision of measurements arising from wetting experiments in practical systems can be low since there are a number of difficult to control factors that af-
2.1. Introduction to glass-to-metal sealing

Figure 2.3: Schematic diagram of a sessile drop showing the liquid - surface contact angle.

ffect the results significantly. These include surface roughness, sample impurities and furnace conditions (with oxygen contamination being a particular problem). Thus, there can be a large scatter in the data collected [80]. For example Sobczak et al reported that results for the contact angle of copper on alumina (a non reactive system) ranged, in different studies carried out between 1957 and 1987, from 110° to 170° [98]. The choice of furnace atmosphere, different gasses or a vacuum also effects the contact angle. For example, in the boroaluminate on Ti-6Al-4V, Kovar, Nilo48 or Alloy52 systems wetting is improved in air as compared with vacuum [116].

Roughness affects the contact angle, as shown in Figure 2.4, since the apparent, and measured, angle may not be the actual angle that the liquid contacts the substrate. Roughness can be caused by grain structure, for example differential polishing may create grooves and pits between grains during the polishing process. These defects may be large enough to prevent the advance of the drop thus altering the contact angle. Grain boundary grooving may also occur in metals heated to greater than half their melting point [26]. Using monocrystalline samples with low surface roughness can allow the measurement of contact angles which are repeatable to within less than 5° [26], however, this is not possible for a system
with metal alloys containing a grain structure. Variation in composition across the sample can alter the wettability, as can the presence of impurities which may segregate to the grain boundaries and thus alter the wettability in specific sites.

Figure 2.4: The effect of surface roughness on the measured contact angle in a non reactive system, after Eustathopoulos et al., [26].

2.1.5 Stresses, defects and reasons for seal failure

Contamination

There are a number of factors that can cause defects in seals. Pores may occur if air is trapped in gaps between glass particles during the sealing stage. In addition, gases may be formed by contaminants such as finger print grease, oils and carbon dust from graphite jigs. Care must be taken to clean and degrease components prior to manufacturing the seal. The formation of gas can occur as a result of redox reactions between the metal and glass as well as by reaction with any carbon or carbides on the surface of the metal. Gases may also diffuse into the metal whilst it is at high temperature and then be forced out of solution as the metal is cooled [113]. Water dissolved in the glass, as molecular water or hydroxyl ions, may also react with the metals, forming hydrogen gas [17]. This can be resolved by producing the glass under dry conditions or by using additions in the glass that react preferentially with the water and do not form gasses [24].
2.1. Introduction to glass-to-metal sealing

Stresses and cracking

As mentioned earlier, there is normally a difference in CTE between the glass /
glass-ceramic and the metal, and this inevitably leads to residual stresses since
the seal is always manufactured at elevated temperature. The magnitude of the
stresses can be controlled, by selecting components with appropriate CTE, but
they will always be present to some degree.

Since the glass should be a low viscosity liquid, at the sealing temperature, there
are no stresses as the glass can easily be displaced. However, as the seal is cooled
it will reach the set point, $T_{\text{set}}$, the point at which it begins to behave like a solid
and is therefore not able to deform and eliminate stress. $T_{\text{set}}$, like $T_g$, is not a
fixed temperature, and it can either be taken as the strain point or annealing
point of the glass, or some temperature close to these [25]. There is no accepted
choice of how to define $T_{\text{set}}$ within the literature.

A schematic diagram of a glass and a metal expansion curve is shown in Figure 2.5.
Since the glass can not flow once it is cooled below $T_{\text{set}}$ the glass expansion curves

![Thermal expansion curves for a glass and a metal, showing the effect on the glass expansion curve of being fixed at $T_{\text{set}}$, resulting in an offset in the glass curve. This gives an idea of the stresses induced in the glass, after Donald [25].](image)

Figure 2.5: Thermal expansion curves for a glass and a metal, showing the effect on the glass expansion curve of being fixed at $T_{\text{set}}$, resulting in an offset in the glass curve. This gives an idea of the stresses induced in the glass, after Donald [25].
must be fixed to intersect at $T_{\text{set}}$, giving an offset in the glass expansion curve. A schematic diagram of the displacement of the expansion curve of a glass sealed in a metal housing is shown in Figure 2.5.

For seals with a metal mounted in glass which is surrounded by a metal cylinder, a common model for seals, there are a number of different effects that can be seen due to high residual stresses [25]. These are listed below:

1) the CTE of the housing > CTE of the glass. This is desirable, since the glass is in radial compression, except if the CTE difference is too great, in which case the glass may spall away from the metal due to circumferential tension, as in Figure 2.6 part a.

2) the CTE of the housing < CTE of the glass. The glass is under radial tension, and therefore liable to crack. It may crack in the glass or at the interface. As in Figure 2.6 part b.

3) the CTE of the pin > CTE of the glass. The glass near the pin is put under radial tension and may crack near the pin, circumferentially, or the glass to metal interface may fail.

4) the CTE of the pin < CTE of the glass. The glass is put under circumferential tensile stress and may crack. As in Figure 2.6 part c.

Approximations for the stresses in cylindrical seals, with or without pins, can be calculated using the CTEs, elastic moduli and Poisson’s ratios of the metals and glasses, [25] or for more detail see [90]. When considering glass-ceramics, the system is generally more complicated since they have more complex expansion curves, sometimes non-linear, due to the presence of various crystal phases.

Stresses may also be created by the formation of interfacial layers, with different CTE than the bulk glass / glass-ceramic. Although these stresses can be
2.1. Introduction to glass-to-metal sealing

Figure 2.6: Thermal expansion curves for a glass and a metal, showing the effect on the glass expansion of being fixed at $T_{set}$, resulting in an offset in the glass curve. This gives an idea of the stresses induced in the glass, after Donald [25].

Calculated the properties of the interface layer must be known, and often they are not [93]. Some information on the stresses can be found using thin strips of metal with glass bonded to them. Like a bimetallic strip, they will bow due to the stresses [52]. Although it is clear that higher residual stresses will result in greater bending, quantitative analysis of the stress at the interface is not possible since any effects are averaged out over all of the glass present and along the whole length of the interface. Finite element analysis could provide detailed information on the stress at particular positions on the interface but again detailed material
information, that is often difficult to obtain or determine, is required [25]. Raman spectroscopy could be used to measure the stresses near the surface.

It has also been noted that the microstructure of a glass ceramic may be altered by the presence of a metal housing, even without diffusion of species between the glass and metal, which may be due to the compressive stresses introduced [3].

2.1.6 Interfacial reactions

As discussed earlier in section 2.1.5, the CTE of the components must not create adverse stresses in the seal. However, reactions at the interface may create reaction products that have significantly different CTE than the glass or metal either side and this create higher stresses than expected. This is one of the problems with the silicides formed when silicate glasses are sealed to titanium alloys. Metal species may also diffuse into the glass and react with any nucleating agents that have been used to control the crystal structure of a glass-ceramic. This may result in the area near the metal containing a greater proportion of glass than the rest of the glass-ceramic, thus altering its CTE which may be deleterious to the seal quality. Since the glass-ceramic used in this project crystallises from the free surface, no nucleating agents were used.

2.2 Materials used in this project

2.2.1 Ti-6Al-4V

Titanium has many benefits as an engineering material; in particular it offers low density 4.5 g cm$^{-3}$, high strength to weight ratio and good corrosion resistance in bulk [57]. Titanium is also of interest for medical implants since it is inert and non
2.2. Materials used in this project

toxic in the human body [53]. For dental applications a ceramic coating is needed for cosmetic purposes [36] and therefore the dental community has undertaken research into the coating of titanium with dental porcelain [32, 73, 75, 86].

Commercially pure titanium exhibits a phase transformation (which causes a volume change) from the low temperature $\alpha$ phase (hexagonal close packed) to $\beta$ (body centered cubic) as it is heated above 882 °C. The exact temperature of the transition is strongly affected by the presence of other elements since they can stabilise either of the two phases - the two most important being oxygen which is an $\alpha$ stabiliser and hydrogen which is a $\beta$ stabiliser [21]. Deliberate alloying additions can also be made to stabilise one or both of the phases, which will alter the microstructure and properties of the alloy as well as moving the temperature at which the $\alpha$-$\beta$ transition occurs and allowing higher temperature operation. Some $\alpha$ stabilisers include aluminium, gallium, germanium, carbon, oxygen and nitrogen, whilst $\beta$ stabilisers include vanadium, iron, cobalt, nickel, manganese, molybdenum and copper. Zirconium, tin and silicon do not promote either phase [84].

The most commonly used titanium alloy is Ti-6Al-4V (IMI318) which contains 6 wt. % aluminium and 4 wt. % vanadium as the alloying elements, creating an $\alpha + \beta$ alloy. Vanadium is a $\beta$ stabiliser whilst aluminium is an $\alpha$ stabiliser [21].

The microstructure of $\alpha/\beta$ titanium alloys is, as would be expected, dependent on the processing. For a more detailed treatment than will be given here please refer to [117, 21, 57, 84]. For annealed Ti-6Al-4V there are two possible structures, corresponding to either cooling from the $\beta$ or $\alpha + \beta$ phase fields. When cooled from the $\beta$ phase the $\alpha$ usually forms in Widmanstätten laths in the $\beta$ matrix. Cooling rate effects the size of the laths. If the alloy is annealed in the $\alpha + \beta$ phase field (usually around 700 °C) prior to cooling to room temperature an equi-axed
microstructure is formed, with grains of $\alpha$ and grains of $\beta$. The $\beta$ grains then transform to Widmanstätten $\alpha$ as they are cooled.

Titanium oxidises rapidly in air to produce TiO$_2$, which has a tetragonal rutile crystal structure [57]. Oxygen can diffuse through the oxide layer which grows at the metal - oxide interface. It is common to suggest pre-oxidising metals prior to glass to metal sealing, however if this is done there is always the concern that the oxide layer may not fully dissolve into the glass during sealing and become a point of weakness if it is not well adherent to the bulk metal. This issue exists with titanium, and as such usual practice is not to pre-oxidise titanium. The titanium used in this project was not pre-oxidised, though there could be scope for some investigation of the effects of pre-oxidation in future.

Short firing times and preoxidation temperatures below 800 $^\circ$C are said in the literature to give good oxide adherence whilst higher temperatures give a weakly adherent scale [43, 2, 120]. Longer firing times, probably associated with thicker oxide layers, have also been shown to reduce the bonding strength of porcelain to titanium [35]. Others have suggested firing in an argon atmosphere to reduce the build up of a non adherent titanium oxide layer, but using shorter firing times is an easier option [68].

Some work has been undertaken using bend testing to assess the titanium-glass/porcelain adherence following different preoxidation schedules. Adachi et al. found that pre-oxidation at 750 $^\circ$C resulted in a greater area of porcelain remaining on the Ti-6Al-4V after fracture than pre-oxidation at 1000 $^\circ$C [2].

This indicates that bonding was stronger with the lower temperature, which also gave a stronger oxide adherence to the bulk. Guo et al. [31] also carried out three-point flexure bend tests on commercially pure titanium coated with SiO$_2$ and found that pre-oxidising the titanium did not result in a stronger bond and
that the failure in the pre-oxidised samples was at the interface between titanium and its oxide. They suggest this is due to the stresses induced by the lattice mismatch of the rutile titanium oxide and the bulk.

2.2.2 Kovar

Nickel-iron alloys are widely used in glass-to-metal seals for electrical feedthroughs since they are good electrical conductors and have tailorable CTEs ranging from $16.7 \times 10^{-6} \, \text{K}^{-1}$ (over 30-850 °C) for pure iron down to $2.6 \times 10^{-6} \, \text{K}^{-1}$ (over 0-200 °C) for Invar and back up to $13.2 \times 10^{-6} \, \text{K}^{-1}$ (up to 420 °C) for pure nickel, as shown in Figure 2.7. Although there are a wide range of iron-nickel alloys only Kovar is studied in this project. Kovar was chosen for its CTE which is similar to that of glass-ceramic chosen.

Kovar, a trademark of Carpenter Technology Corporation, is an iron-nickel-cobalt alloy, the composition of which is given in Table 2.3. Kovar conforms to the ASTM F-15 standards (F01 Committee, 2013). Other names for Kovar include Nilo-K, Nicoseal, Rodar, Telcoseal, Sealvar, Dilver, Pernifer2918, Alloy 29-17, DIN 17745, AFNOR NF A54-301 and SEW 385 [25].

Kovar has a coefficient of thermal expansion similar to that of a hard borosilicate glasses such as Pyrex so it is suitable for sealing to these glasses. An expansion curve is given in Figure 2.7.

It is usual to pre-oxidise Kovar prior to sealing in a glass-to-metal seal; the literature surrounding the growth of oxide layers on Kovar and their effect on sealing is explored in detail in Section 2.4.
2.2.3 Glass-ceramics

Glass-ceramics are defined by McMillan as “polycrystalline solids prepared by the controlled crystallisation of glasses” [67]. Donald Stookey is credited with their discovery, and early development, whilst working at Corning Glass Works on photosensitive glasses [101, 102, 103, 104]. During their development, glass-ceramics were known by a number of names, sitalls in the Soviet literature, pyrocerams in the USA and vitrocerams in Germany [115], names which remain as trade names.

The crystallised glass contains a great number of small crystals, which are homogeneously distributed, with some residual glass left binding crystals together.

| Table 2.3: Nominal molar composition of SRBAL glass. |
|----------------|----------------|----------------|----------------|----------------|
| Fe  | Ni  | Co  | C   | Mn | Si  |
| Bal.| 29  | 17  | 0.02 max | 0.3 max | 0.2 max |
The crystalline fraction can vary from 20-99 % [115] but is usually 90-98 % [25]. Crystal size is typically less than 10 µm but can be as low as 10-20 nm [61].

Glass-ceramics have a range of unique and interesting properties, some of which can be beneficial when creating materials for sealing. They are more refractory than glass, have controllable CTE, have generally improved mechanical properties, resist chemical attack better than glass and can be made into complex shapes using glass forming techniques [23, 96]. Other potential properties and uses include ionic conductivity [108], optical nonlinearity [60, 107] semiconducting properties [62] and making transparent armour [29, 81].

In order to tailor the CTE, different crystal phases must be formed. For example in the LAS system (i.e. glasses containing Li₂O, Al₂O₃ and SiO₂) the CTE can be low, zero or negative depending on the crystallisation used [40, 97]. Low expansion aluminoborate glasses can also be made [58, 109].

To create a glass ceramic a two step heating cycle is usually followed. The standard process is discussed below, although it was not followed precisely during the manufacture of the seals studied in this project due to the crystallisation characteristics of the glass chosen.

In the first processing stage the glass is heated, in a solid state, to a temperature where nucleation can occur. Nucleation may be homogeneous or heterogeneous. During the nucleation stage a large number of nucleating sites are formed whilst crystal growth is kept as low as possible. This can be done by holding the glass at a temperature below the crystallisation temperature. Homogeneous nucleation rate increases exponentially with temperature until a point at which it rapidly declines and is replaced by crystallallisation. The exact interplay between the variables and derivations of the relevant relations can be found in [67, 82, 96]. Nucleation can be encouraged by adding a small, less than 10 wt. %, amount of a
nucleating agent. Common nucleating agents include Cu, Ag, Au, AgCl, Cu$_2$O, TiO$_2$ and P$_2$O$_5$ among many others [25].

After nucleation the glass is heated to a higher temperature to allow the growth of crystals, [25, 74], resulting in a heat treatment cycle like the one shown in Figure 2.8. The crystal phases formed and their relative proportions will depend on the exact ratio of elements in the glass, the nucleating agents used and the heat treatment schedule. If the glass-ceramic is to be used in a glass to metal seal an extra stage is added to the heat treatment cycle. The glass is first melted so that it can flow and wet the metal, then the nucleation and crystallisation stages are followed to form the glass-ceramic. It must be remembered that the heat treatment may alter the properties of the glass and may change the interfacial reactions and alter the hermiticity of the seal [24, 25]. Therefore, before creating any seals, testing of the exact compositions and heat treatment should be undertaken. If the glass has crystallised during production then it may be necessary to heat to high temperatures, 1000 °C or more, in order to melt the crystals [6]. This may alter the microstructure and properties of the metals being used, or may not be possible depending on the particular metal.

Differential thermal analysis (DTA) and differential scanning callorimetry (DSC) can be used to determine optimum heat treatment schedules. Sharp exothermic peaks are associated with the formation of crystal phases, multiple peaks indicating that multiple different crystals are being formed. Examples of a DTA and a DSC trace for a lithium zinc silicate glass are shown in Figure 2.9. Additionally, an endothermic reaction occurs when the crystals melt. Combining this with information on CTE, from dilatometry, allows the appropriate temperature for crystallisation to be determined. Dynamic mechanical analysis is also useful for finding the glass transition temperature of residual glassy phase [25]. The results of these techniques are very dependent on the parameters used during testing [22].
2.2. Materials used in this project

2.2.4 Borate glasses

The structural models for boric oxide and glasses based upon it are significantly different to those for silica. Boron can form both trigonal planar and tetrahedral structures, and does so in crystalline compounds, but in vitreous boric oxide it forms only triangular structures. It is generally stated that the resultant large scale structures are therefore planar, with any morphology in the third dimension being due to folding of this two dimensional plane. This explains the low \( T_g \) of vitreous boric oxide, \( \sim 260 \, ^\circ\text{C} \) compared with \( \sim 1100 \, ^\circ\text{C} \) for vitreous silica. The constituent boron and oxygen atoms tend to form boroxol rings, shown in Figure 2.10, formed from three boron atoms and three oxygen atoms. These rings

Figure 2.8: The heat treatment schedule specified in Stookey’s early patent for making “semicrystalline ceramic bodies”, as glass ceramics were initially known. (After Stookey [104]).
can bend such that they extend out of the plane and the B-O-B (boron to oxygen
to boron) bond angle is varied. However, there is literature showing that other,
3-dimensional, structures can form in B$_2$O$_3$ [106, 28].

Figure 2.9: Representative DSC and DTA traces for a lithium zinc silicate glass,
(after Donald [22]).

Figure 2.10: Schematic diagram of boroxol rings and the B-O-B angle, as found
in vitreous boric oxide and alkali borate glasses, after (Shelby, [96]).
2.2. Materials used in this project

In silicate glasses adding alkali or alkaline earth oxides (such as the SrO used in the SRBAL glass used in this project) creates non-bridging oxygen (NBO). In borate glasses the addition of these oxides cause a trigonal borate group to change to a tetrahedral borate group because the oxygen from the added oxide is incorporated into the boron tetrahedron. The tetrahedra created have negative charge that is balanced by the alkaline earth ion, ensuring local charge neutrality. This increases the connectivity of the network and increases $T_g$ whilst decreasing CTE. This trend continues up to a concentration of 30 mol % of alkali / alkaline earth. Above 30 mol. % the number of tetrahedral units is reduced as negatively charged trigonal borate groups begin to be formed. This model is not sufficient to explain all the properties of alkali borate glasses since other structures are formed at higher alkali content. The boroxol rings can have one of their triangles converted to a tetrahedron (known as a tetraborate unit) or two tetrahedra (known as diborate groups). Even higher additions of alkali oxides cause NBO to be formed. The interplay of these structures is shown in Figure 2.11, though this is a simplified model that does not fully explain the observed variations in the properties of borate glass.

Little work has been reported on borate-based glass-ceramics but they are generally believed to crystallise from the surface [25]. If glass powders are used to make glass-to-metal seals, nucleation occurs at the surfaces of the glass and as such a nucleation stage of the glass-ceramic production process is not necessary. The glass needs only to be heated to it soften, before being cooled. Crystallisation will occur without the need for a nucleation stage as the surfaces act as nucleation sites. If a single amorphous glass piece was used then crystallisation would be expected to proceed from the surface. The resulting large crystals would be weak and would also weaken the seal by causing stress concentration at their interfaces.
The SRBAL glass composition used in this project, given in Table 3.2, was introduced in the 1980s by Moddeman et al. [69] but little work has been reported on it since. Its composition and properties are given in 3.2, as reported by Brow et al.. SRBAL has been shown to bond to titanium and its alloys [9, 6]. The bonding of borate glasses, including SRBAL is considered further in Section 2.3.2 “Sealing titanium to borate-based glasses”.

Table 2.4: Compositions, in mol. %, and properties of SRBAL glass [6, 9].

<table>
<thead>
<tr>
<th>Glass</th>
<th>Al₂O₃</th>
<th>B₂O₃</th>
<th>CaO</th>
<th>SrO</th>
<th>BaO</th>
<th>CTE</th>
<th>T₉</th>
<th>Tₓ</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRBAL</td>
<td>15</td>
<td>40</td>
<td>-</td>
<td>45</td>
<td>-</td>
<td>9.8</td>
<td>570</td>
<td>800</td>
</tr>
</tbody>
</table>
2.3 Sealing glasses to metals

2.3.1 Sealing titanium to silicate glasses

There are a number of problems with using titanium in glass to metal seals. Firstly, the common silicate based sealing glass compositions are not generally suitable for use with titanium. Titanium can diffuse into the glass at concentrations of up to 20 at. %, [24], allowing the formation of interfacial titanium silicates which are brittle and poorly adherent [25]. Ti$_5$Si$_3$ has a thermal expansion that is highly anisotropic, around $6 \times 10^{-6}$ K$^{-1}$ in the a direction and $17 \times 10^{-6}$ K$^{-1}$ in the c direction [92], and its average CTE is also different from the CTE of titanium. The silicide to residual glass interface appears to be where seal failure occurs [6]. A further complication resulting from the formation of titanium silicides is the evolution of oxygen during the reactions creating them, as described by Equation 2.5, causing porosity [37].

$$5Ti_{(metal)} + 3SiO_{2(glass)} \rightarrow Ti_5Si_3_{(interface)} + O_2 \uparrow \quad (2.5)$$

Further complications when sealing to titanium include the volume change at 882 °C (unless an $\alpha$ – $\beta$ alloy such as Ti-6Al-4V is used) and that the oxide layer on titanium does not always adhere well to the bulk, making the seal liable to failure if the oxide layer is thick.

Some success has been reported with silicate containing glasses and titanium or its alloys. Taylor et al. reported using a boroaluminosilicate glass, Pemco 1409P (composition in weight percent of 44% SiO$_2$, 29% B$_2$O$_3$, 14.4% Al$_2$O$_3$, 10.4% MgO, 2.2% CaO) blended in varying amounts with an aluminosilicate glass developed by Sandia National Labs, TA-23 (composition in weight percent
of 44.95% SiO$_2$, 8.0% B$_2$O$_3$, 20.0% Al$_2$O$_3$, 7.0% MgO, 12.0% CaO, 6.0% SrO, 2.0% La$_2$O$_3$, 0.05% CoO).

The blended glasses were sealed in a Ti-6Al-4V ferrule with tantalum pins and the resulting seals were hermetic (He leak test less than $1.0 \times 10^{-9} \text{ cc}^{-1}$) and maintained hermeticity after thermal shock tests. The melting temperature of the glass, its tendency to crystallise or its strength in a pin pull test was not reported [111].

Preoxidising the titanium, with a thick oxide layer of $8 - 10 \mu m$ can also improve sealing by eliminating the reaction of Ti with SiO$_2$ to form O$_2$ gas. However, the poor adherence of the oxide layer to the bulk is still a problem, [24].

Pre-nitriding has also been proposed though porosity may still occur through the reaction in Equation 2.6:

$$5TiN_{(interface)} + 3SiO_2_{(glass)} \rightarrow +Ti_5Si_3_{(interface)} + 3O_2 \uparrow +5/2N_2 \uparrow \quad (2.6)$$

However, Brow and Watkins reported a pre-nitriding stage, which eliminated the interfacial silicides and produced a very strong seal with good adhesion [10]. A comparative seal using pre-oxidised titanium was very weak, as expected. Taylor et al. describe methods for sealing and suggest that lead borosilicate, borosilicate or boroaluminosilicate glasses would be suitable for sealing to pre-nitrided titanium [110]. Others have also suggested using coatings of titanium compounds, for example Sviridov suggests that TiB$_2$ and TiSi$_2$ are stable at 1000 °C whilst in contact with a glass of composition 20 mol % Na$_2$O, 10 mol % Al$_2$O$_3$, 70 mol % SiO$_2$, though they did not attempt to make a practical coating or seal with a TiB$_2$ or TiSi$_2$ coating [105]. This does not seem to have become a popular area.
and research has instead continued into using silicate free glasses.

The addition of other oxides to the glass can also be used to prevent gas forma-
tion. Donald [25] references work by Hong stating that adding CoO to silicate
glasses results in the reaction shown in Equation 2.7 occurring preferentially to
the reaction in Equation 2.6.

\[ Ti_{(metal)} + 2CoO_{(glass)} \rightarrow 2Co_{precipitate} + TiO_2(glass) \]  (2.7)

The cobalt precipitates may also improve bonding, through mechanical keying,
and the seals were found to fail in the glass-ceramic rather than at the interface.

### 2.3.2 Sealing titanium to borate-based glasses

There has been an interest in using borate-based glasses to seal to titanium since
they can be made without the inclusion of the silicon, and the titanium silicides
that are formed when silicon reacts with titanium. However, there is not a large
body of literature on borate-based glass-ceramics.

Donald *et al.* produced lithium borate glasses but failed to process them into
high strength glass-ceramics, which they proposed was due to the crystallisation
beginning at the surface of the glass [22].

When used for sealing, borate glasses still react with titanium, forming titanium
borides, but the borides may be beneficial for joining rather than deleterious as
silicides are. The reaction is slower than for silicon, so a much smaller volume
of interfacial reaction products forms than with silicate glasses. Additionally,
the CTE of the borides is more similar to titanium than the silicides; TiB₂ has
a thermal expansion at 500 °C of around 7 × 10⁻⁶ K⁻¹ in the a direction and
10 × 10⁻⁶ K⁻¹ in the c direction [71].
Chapter 2. Literature Review

Brow has done work in the area of borate based glasses and glass-ceramics which show promise for sealing to titanium. Brow and Watkins introduced alkaline earth-aluminoborate glasses containing CaO, Al$_2$O$_3$, B$_2$O$_3$, SrO and BaO designed for sealing to titanium in 1992 [9]. The composition of these glasses is given in Table 2.5. The lack of silicon means no interfacial silicates will be formed, no gasses are observed to be evolved during sealing and the CTEs are $9.1 \times 10^{-6}$ K$^{-1}$ which is in the same range as titanium alloys. The seals created were 50-100% stronger than those made with a commercial glass, Kimble TM-9 which is an alkali-silicate glass.

Table 2.5: Compositions, in mol. %, of four boroaluminate glasses, data from [6, 9].

<table>
<thead>
<tr>
<th>Glass</th>
<th>Al$_2$O$_3$</th>
<th>B$_2$O$_3$</th>
<th>CaO</th>
<th>SrO</th>
<th>BaO</th>
<th>CTE</th>
<th>T$_g$</th>
<th>T$_x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CABAL-17</td>
<td>20</td>
<td>30</td>
<td>50</td>
<td>-</td>
<td>0</td>
<td>9.1</td>
<td>592</td>
<td>805</td>
</tr>
<tr>
<td>SrBAL-1</td>
<td>15</td>
<td>40</td>
<td>-</td>
<td>45</td>
<td>-</td>
<td>9.8</td>
<td>570</td>
<td>800</td>
</tr>
<tr>
<td>BABAL-2</td>
<td>20</td>
<td>40</td>
<td>-</td>
<td>-</td>
<td>50</td>
<td>10.4</td>
<td>543</td>
<td>-</td>
</tr>
<tr>
<td>BABAL-1C</td>
<td>10</td>
<td>40</td>
<td>30</td>
<td>-</td>
<td>20</td>
<td>10.1</td>
<td>558</td>
<td>-</td>
</tr>
</tbody>
</table>

This work was improved upon by Brow et al. by adding La$_2$O$_3$ to the glasses to make barium lanthanoborate glasses (CTE $8.7 - 10.3 \times 10^{-6}$ K$^{-1}$) with improved dissolution rates compared with the CABAL, SRBAL and BABAL glasses detailed in Table 2.5 [7]. It should be noted that these glasses are not suitable for sealing at high temperatures. Crystallisation into a glass-ceramic during a sealing cycle may increase the melting point, but the properties of the glass-ceramic were not reported.

In the same report Brow et al. also developed an empirical formula, given in Equation 2.8 for the CTE of glasses containing La$_2$O$_3$, TiO$_2$, Al$_2$O$_3$ and CaO.
2.3. Sealing glasses to metals

\[
CTE = (0.318 \times B_2O_3) + (1.65 \times La_2O_3) + (0.865 \times TiO_2) - (0.396 \times Al_2O_3) + (1.70 \times CaO) + (0.0394 \times La_2O_3 \times Al_2O_3)
\] (2.8)

This may be a useful starting point when designing and choosing glasses for sealing to metals, so that CTE can be tailored to give matched or compressive seals.

Donald [24] states that Brow and Watkins have successfully sealed CABAL, SR-BAL and BABAL glass to titanium. Titanium was detected up to 15 µm into the glass by energy dispersive x-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS) indicated that a titanium borate may have been formed by the below reaction in Equation 2.9:

\[
5Ti_{(metal)} + 2B_2O_3_{(glass)} \rightarrow 2TiB_2_{(interface)} + 3TiO_2_{(interface)}
\] (2.9)

The borates that do form are thought to be dendritic which may help increase seal strength through roughening of the interface and increased mechanical keying [6, 89] as compared with titanium silicides which are planar. Since the borate glasses are less reactive than silicates the borides formed may create a layer that slows the formation of further borides.

Saha [89] used XPS, scanning electron microscopy (SEM) and wavelength dispersive x-ray spectroscopy (WDX) to investigate the reactions between titanium metal and B$_2$O$_3$ melt glass. B$_2$O$_3$ glass was fractured in high vacuum and then 3 nm of titanium was deposited whilst maintaining high vacuum and XPS analysis carried out before titanium deposition, after deposition, and again after heating the sample to 400 °C. Diffusion couples were also prepared and held at between
500 °C and 1000 °C and from 1 hour to 48 hours. Boron-rich high aspect ratio dendrites were observed to have grown into the titanium (as seen in back-scattered electron images and WDX maps) in diffusion couples prepared at 1000 °C but were not observed (possibly because of their small size) in samples prepared at 800 °C and 500 °C. XPS shows that the as deposited surface, prior to heating, contained titanium boride. It was presumed to be TiB₂, since it is the most stable titanium boride, however the peaks could not be resolved sufficiently precisely to give complete confidence in the identification. The proposed reaction is given in Equation 2.10.

\[ Ti + xB_2O_3 \rightarrow TiB_{2x-2} + B_2O_{3-y} + 1/2(y + 3x - 3)O_2 \]  

(2.10)

The reaction products are TiB or TiB₂ and since TiO does not form, there is not a TiO – B₂O₃ interface so there can not be a region of glass saturated with metal oxide, as is usually suggested as the optimum bonding condition. It is instead necessary to consider the strength of Ti - Ti borate and Ti borate to borate glass interfaces. The titanium boride layer is expected to form immediately and act as barrier to diffusion of titanium into the glass.

Since the titanium borides formed at the interface are believed to be dendritic, unlike titanium silicides, mechanical keying is also believed to play a role in determining the strength of this interface. This is thus a contributing factor in the success of sealing borate glasses to titanium. The titanium borides were observed to grown from the interfacial layer into the titanium side of the interface.
2.3. Sealing glasses to metals

2.3.3 Sealing glasses and glass-ceramics to Kovar

A number of best practices have been established for the use of Kovar, such as cleaning and pre-oxidising, and their parameters have been investigated in order to optimise seal production. According to the Carpenter Technology Corporation online data sheet “all degreased, fabricated Kovar alloy parts should be degassed and annealed in a wet hydrogen atmosphere” [33]. When sealing, the heating should be in the range of 838 - 1099 °C, for two hours at the lower temperatures down to 20 minutes for the higher temperatures. For preoxidation it is suggested that, as is consistent with other literature, “the best oxide film is thin and tightly adhering” which can be achieved by heating to 650 - 700 °C in air and a good layer will be a “dark gray to slight brown oxide”.

Special Metals Corporation, manufacturers of NILO K (a trade name for Kovar), state that, prior to sealing, decarburization can be “carried out in an atmosphere of wet hydrogen at 900 - 1050 °C for 1 hour” and that if an oxide layer is required the NILO K “can be oxidized by heating in air to temperatures in the 600 - 1000 °C range, depending on the thickness of oxide film required”.

The composition of the oxide can be altered by the choice of oxidising conditions but is generally reported to be some combination of FeO, Fe₂O₃, and Fe₃O₄ though some authors also report (Fe,Co,Ni)₃O₄ phases. A full review of the relevant literature on composition of the oxide layer on Kovar is given in the next section, Section 2.4, and the results of experiments carried out as part of this thesis are given in Chapter 4.

A range of times, temperatures and oxidising atmospheres are recommended but an oxide thickness of somewhere between 2 µm and 8 µm or 0.3 to 1 mg cm⁻² is generally recommended as oxides in this range have been shown to produce successful seals [1, 16, 54, 66, 77].
Pre-oxidising of metal parts is often used to improve bonding and wetting and is common practice with Kovar, where pre-oxidation improves wetting with a range of glasses [25]. Wei studied the same glass that was used in this project (SRBAL) and found the wetting of Kovar to be improved by pre-oxidation [116]. Some of the early work by Pask and co-workers ascertained that pre-oxidising iron improved wetting and adherence [79]. Borosilicate glasses have been shown to wet pre-oxidised Kovar [16, 56].

When pre-oxidised Kovar is sealed to glass, the oxide dissolves (partially or fully) and metal ions enter the glass. This creates the conditions described in Figure 2.2 where metal-metal bonding can occur across the interface. It also alters the properties of the glass or glass-ceramic in the area where diffusion has occurred. For example, Zanchetta et al. describe four regions that make up the interface after sealing: the original Kovar, an iron depleted region $\sim 8 \, \mu m$ thick, a glass and (probably dissolved) iron oxide region $\sim 2 \, \mu m$ thick and finally a region $\sim 30 \, \mu m$ think where iron had diffused into the glass. The CTE of their glass is raised by the addition of iron oxide as is the CTE of the metal by the reduction in iron, so that the CTE across the interface is roughly continuous. This condition is only met for sealing times chosen such that the oxide has fully dissolved into the glass but has not diffused away from the interface. Chanmuang et al. also report porous iron depleted region and region of glass containing diffused iron as do many others [14].

2.4 Pre-oxidation of Kovar and similar alloys

As mentioned above, it is common practice in industry to pre-oxidise Kovar prior to sealing, and suppliers recommend pre-oxidation [33]. However, the literature regarding the oxidation mechanisms and products is limited and contradictory.
Different authors report different oxides and many make only a basic attempt to explain the processes that could have formed the oxide. There is also a tendency to carry out the oxidation experiments on plates of Kovar, with varying surface finishes, despite the common application of Kovar pins in electrical feed through seals.

In the existing literature there are many different oxidising atmospheres used; a summary is given in Table 2.6. Although the experiments in this thesis were only carried out in air, all of the variations in atmosphere are considered in the literature review.

Table 2.6: Examples of the wide range of oxidising conditions for Kovar oxide growth.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>Chern and Tsai [16]</td>
</tr>
<tr>
<td>Dry air</td>
<td>Chern and Tsai [16], Piscitelli et al. [83], Stephens et al. [100], Chanmuang et al. [14]</td>
</tr>
<tr>
<td>Purified air</td>
<td>Abendroth [1]</td>
</tr>
<tr>
<td>Steam and carbon dioxide</td>
<td>Klein [49]</td>
</tr>
<tr>
<td>Nitrogen plus water and hydrogen</td>
<td>Luo and Shen [56]</td>
</tr>
</tbody>
</table>

Abendroth reported that the oxide was variously FeO, Fe$_2$O$_3$ or Fe$_3$O$_4$ depending on oxidising conditions, temperature and cooling parameters [1]. Abendroth mentioned the possibility of the oxide containing the spinel of CoFe$_2$O$_4$, but decided that the evidence to support it was not strong enough. Within the uncertainty of the XRD data, it could not be decisively concluded whether the phase was Fe$_2$O$_3$ or CoFe$_2$O$_4$ and since the activation energy of the spinel phase was significantly greater than the observed activation energy in the experiments it was concluded that CoFe$_2$O$_4$ was not present.

Some later work by Piscitilli did conclude, based on XRD data, that the spinel was present [83]. This work found that the oxide was 100% spinel when oxidised...
for 4 minutes at 900 °C or 850 °C. Spinel content decreased as oxidation temperature decreased from 900 °C down to 787 °C and oxidation time increased from 4 minutes to 20 minutes giving a mixture of CoFe$_2$O$_4$ and α–Fe$_2$O$_3$. Spinel content ranged from 100 - 66.5% in the samples treated at 787 °C for 20 minutes (the longest and coolest conditions used).

The possibility of the spinel has subsequently only been mentioned by a minority of the papers on Kovar oxidation. Luo and Shen aimed to produce an oxide of Fe$_2$O$_3$ by controlling oxygen partial pressure [56]. They mentioned that the cell spacing, $a_0$, of their oxide is greater than expected but later dismissed the possibility of spinel due to lack of cobalt in the oxide layer. de la Rama et al. mentioned the presence of cobalt in their oxide layer but continued to refer to it as simply Fe$_2$O$_3$ and Fe$_2$O$_3$ even after they have reported it to contain up to 15 at. % cobalt [20].

Klein et al. carried out Auger spectroscopy and depth profiling following oxidation at 485 °C but reported no cobalt or nickel at the sample surface; this may be due to the low oxidation temperature used [49]. Other authors have also reported simple iron oxide layers. Chern and Tsai reported an FeO layer but concern themselves mainly with the thickness and adherence of the oxide rather than confirming by experiment that the oxide was indeed FeO [16]. Chanmuang et al. reported FeO, Fe$_2$O$_3$ and Fe$_2$O$_3$, identified by XRD, and state that, as CoO and NiO are less thermodynamically favourable than FeO and Fe$_2$O$_3$, then Co and Ni would not be involved in the oxide layer [14]. Given that others have shown experimentally that Co, and to some degree Ni, are present in the oxide and that the oxide growth is kinetically controlled this conclusion seems misplaced. Yext et al. made no attempt to assess the type of oxide formed, instead assessing only its thickness and reproducibility [119].
2.4. Pre-oxidation of Kovar and similar alloys

2.4.1 Oxides on other iron, nickel, cobalt alloys

In addition to the various studies on Kovar there are a number of papers on other Fe, Ni, Co alloys that are of use when considering Kovar. Mayer and Smeltzer oxidised Co-Fe alloys with 0-70% wt.% Fe at 1200 °C and reported the oxide to consist of (Co,Fe)O or (Co,Fe)O plus (Co,Fe)$_3$O$_4$ depending on oxygen partial pressure and Fe content of the alloy [64]. One recent and comprehensive paper by Chapman et al. considered a variety of Fe, Ni, Co binary and ternary alloys, and reported the presence of (Co$_x$Fe$_{3-x}$O$_4$) and (Ni$_x$Fe$_{3-x}$O$_4$) in ternary Fe, Ni, Co alloys oxidised at 800 °C in air, as identified by XRD [15]. Kim et al. looked at Invar, Fe-30%Ni-12.5%Co, oxidised in air at 1000 - 1200°C for 10 hours reported a complex five-layered oxide with the surface layer containing mixed CoFe$_2$O$_4$, Fe$_2$O$_3$ or CoFe$_2$O$_4$ with a Fe$_2$O$_3$ layer below, identified by XRD [45]. Wu et al. looked at Fe-Ni-Co superalloys and found a cobalt enriched layer on the surface of the oxide following oxidation in air for several hundred hours, which they described as cobalt dissolved in Fe$_3$O$_4$. They make no mention of CoFe$_2$O$_4$ spinel, although this phase could be consistent with their data [118].

2.4.2 The effect of time, temperature and surface finish

Although the standards for Kovar specify a maximum grain size, [27], it may vary and can affect the rate of oxide growth [50, 83]. There is evidence that grain boundaries are a fast path for diffusion in nickel [5], and many authors report porosity along grain boundaries following oxidation that is indicative of diffusion occurring preferentially along grain boundaries [15, 45, 55, 83]).

Throughout the literature a wide range of times and temperatures are investigated. Many researchers use a certain thickness of oxide as their target, or a
certain weight gain such as 0.0003 to 0.0007 g/cm\(^2\) as recommended by Pask [77], who also suggested that the oxidation temperature was not as important as the thickness and adherence of the oxide. A recommendation of oxidation schedules of 17 minutes at 800 °C, 3 minutes 900 °C, 1 minute at 1000 °C or 1/4 minute at 1100 °C was made. However, there is evidence to suggest that the oxidation temperature does affect the formation of the oxide and the oxide species that are formed [83, 100]. Stephens suggests that there is a transition from the formation of Fe\(_2\)O\(_3\) to spinel (Fe, Ni, Co)\(_3\)O\(_4\) at around 750 - 790 °C. This is in broad agreement with Piscitelli’s observation that spinel content decreased as oxidation temperature decreased. Abendroth notes that the activation energy for the oxidation changes at around 800 °C, being 241 kJ mol\(^{-1}\) (reported as 57.6 Kcal) below 800 °C and 129 kJ mol\(^{-1}\) (reported as 30.9 Kcal) above 800 °C [1]. In addition, Chern and Tsai noted that the oxidation rate was much higher at 900 °C than at 700 °C or 800 °C, further evidence that the oxide formed may be different [16]. The literature indicates that the oxide formed depends on the temperature and contains increased (Fe, Co, Ni)\(_3\)O\(_4\) above about 800 °C.

### 2.4.3 CoFe\(_2\)O\(_4\) and NiFe\(_2\)O\(_4\) spinel in the Kovar oxide layer

Although there are a range of results reported in the literature, there are a number of authors who, having considered the data closely, conclude that the oxide is more complex than many assume and its composition may be dependant on oxidation temperature. Some well considered papers report the presence of CoFe\(_2\)O\(_4\) spinel in the oxide. This is of significance for glass-to-metal sealing using Kovar as it is often assumed that the oxidation temperature used is not particularly important even though it may affect the type of oxide formed. The presence of cobalt in the oxide may affect the bonding of glass to the Kovar due to differences in the
solubility of cobalt compared with iron in glass, or altered dissolution of iron from the CoFe$_2$O$_4$ spinel as opposed to Fe$_2$O$_3$. A review of the literature surrounding (Fe,Co,Ni)$_3$O$_4$ spinels and their identification is given here as it will be needed when considering the results in Chapter 4.

2.4.4 Structure of CoFe$_2$O$_4$ and NiFe$_2$O$_4$ spinels

Fe$_3$O$_4$ has an inverse spinel structure and contains both Fe$^{3+}$ and Fe$^{2+}$ cations. The Fe$^{3+}$ ions fill the tetrahedral lattice sites and half of the octahedral sites. The remaining half of the octahedral sites are filled by the Fe$^{2+}$ ions. Fe$_3$O$_4$ is predicted to have five Raman active bands, and four infrared-active bands, corresponding to different vibrational modes [94]. There is disagreement around the weaker Raman bands, but there is generally agreement within the literature as to the position of the major three bands at around 306 cm$^{-1}$, 538 cm$^{-1}$ and 666 cm$^{-1}$ [94]. When analysing Fe$_3$O$_4$ it is important to realise that the laser may heat the sample to a significant degree and cause degradation and conversion to Fe$_2$O$_3$, with the corresponding Raman bands becoming visible. Since the Raman scattering of haematite is significantly stronger than that of magnetite only a small degree of damage may affect the observed signal. It is known that laser induced damage can change Fe$_3$O$_4$ to Fe$_2$O$_3$ and this must be considered when assessing results in the literature and experimentally.

NiFe$_2$O$_4$ is, like Fe$_3$O$_4$, an inverse spinel, with the tetrahedral sites filled with Fe$^{3+}$ ions. The octahedral sites are half filled with Fe$^{3+}$ ions and half filled with Ni$^{2+}$ [30, 38]. CoFe$_2$O$_4$, however, is a partially inverted spinel, with the cobalt atoms being predominantly on the octahedral sites [114, 11].
2.4.5 Identification of CoFe$_2$O$_4$ and NiFe$_2$O$_4$ by Raman spectroscopy

Although there has been no work, to the author’s knowledge, which uses Raman spectroscopy to characterise the oxide on Kovar the technique has been widely used to characterise the various spinels including (Fe, Co, Ni)$_3$O$_4$ spinels in work studying nanoparticles with tunable properties for catalysis and magnetic properties [13] and in situ characterisation of corrosion [112, 63]. As a result, there are example spectra available and generally accepted positions for the major bands. An example spectra of CoFe$_2$O$_4$ is shown in Figure 2.12 and example spectra of Fe$_3$O$_4$ and Fe$_2$O$_3$ are shown in Figure 2.13. Typically reported literature values for the major Raman active bands in Fe$_3$O$_4$ are given in Table 2.7 to give an indication of the variability in the reported values; no assignment of the bands to particular vibrational modes is given as there is not agreement between the sources on the assignment of the bands to specific modes.

![Figure 2.12: An example Raman spectrum of CoFe$_2$O$_4$ [13].](image)

The presence of peaks and around 470 - 490 cm$^{-1}$ and 695 - 700 cm$^{-1}$ in a sample known to contain a spinel structured oxide with Fe,Ni,Co cations can
2.4. Pre-oxidation of Kovar and similar alloys

![Example Raman spectra of Fe$_2$O$_3$ and Fe$_3$O$_4$][91].

Figure 2.13: Example Raman spectra of Fe$_2$O$_3$ and Fe$_3$O$_4$ [91].

Table 2.7: The major Raman bands for Fe, Ni, Co containing spinels and Fe$_2$O$_3$. Sh denotes a shoulder.

<table>
<thead>
<tr>
<th>Spinel</th>
<th>Ref.</th>
<th>Laser used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_3$O$_4$</td>
<td>183</td>
<td>306 - 538</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>293</td>
<td>- - 531</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>302</td>
<td>- 513</td>
</tr>
<tr>
<td>NiFe$_2$O$_3$</td>
<td>-</td>
<td>460sh, 574sh, 654, 492 595 702</td>
</tr>
<tr>
<td>NiFe$_2$O$_3$</td>
<td>-</td>
<td>457sh, 570, 665sh, 488 592 705</td>
</tr>
<tr>
<td>NiFe$_2$O$_3$</td>
<td>-</td>
<td>483sh, 579, 665sh 490 700</td>
</tr>
<tr>
<td>CoFe$_2$O$_4$</td>
<td>209</td>
<td>311 470 577 624sh, 695</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>227</td>
<td>294 411 500 614 [91] 514.5 nm Ar</td>
</tr>
</tbody>
</table>

thus reasonably be attributed to the presence of CoFe$_2$O$_4$, NiFe$_2$O$_4$ and or a solid solution containing one or both the compounds.
2.5 Conclusions

Having considered the existing literature there are a number of areas that are in need of investigation or further clarification. The literature shows that it is possible to produce an hermetic seal with titanium with several boroaluminate glass compositions. However, the studies that indicate that titanium boride is formed at the interface of a titanium to borate glass seal the work have either been carried out either in a model system, [89], or on samples treated for a much longer time than in normal seal production [6]. Within the existing body of work, the reactions between borate glasses and titanium alloys sealed for normal durations have not been characterised. The work presented in this thesis will aim to address this issue for the case of strontium boroaluminate glasses / glass-ceramics.

The interfacial reactions and sealing best practices with Kovar have been more extensively studied than with titanium. It is generally accepted that Kovar should be pre-oxidised, with an oxide layer 2 - 8 \( \mu \text{m} \) thick being preferred. This oxide is normally expected to dissolve in the glass, creating an iron rich area of glass near the Kovar and leaving a rough or porous surface on the remaining metal. Good bonding can normally be achieved with pre-oxidised Kovar following some optimisation, depending on the glass to be sealed to. There is still a need to characterise and understand the reactions between Kovar, or pre-oxidised Kovar, and the specific glass in this project, SRBAL, which has not been investigated previously.

There is significant variation in reports in the literature on the nature of the oxide when it is pre-oxidised. Some work suggests that the oxide is FeO, Fe\(_2\)O\(_3\) or Fe\(_3\)O\(_4\) while others suggest that there may be (Fe, Co, Ni)\(_2\)O\(_4\) formed in the oxide. Since there is such variation in the literature a part of this work will focus on the study of the oxide formed on Kovar under the conditions used for production of the seals studied in order to confirm the nature of the oxide prior to sealing.
Chapter 3

Seal manufacture and characterisation methods

3.1 Introduction

An overview of the design and manufacture of the seals is given here to provide background and context to the work, though it was not the focus of the project and was performed by others \(^1\). The seals were not the actual components intended for use but instead were a simplified design to enable easier production of samples. Although the focus of this work is the glass-to-metal interfaces, the seal design, manufacture and processing is important as various factors have the potential to affect the interfaces, for example by changing stresses in the seals or by introducing variations in the material properties.

In the second section of the chapter, some of the characterisation that was performed as a part of the early seal design is presented. This work was mainly to

\(^1\)Seal design primarily by Martyn Staff, John Fernie, Phil Mallinson and Faye McCarthy
assess whether or not successful seals had been made and to guide improvement in the processing. It is presented here as, although it was not a major part of the project, it needed to be completed to enable a final seal configuration to be established. Finally the methods used in sample preparation and subsequent characterisation are described.

3.2 Seal components and methods of manufacture

3.2.1 Metal Components

All the seals analysed were Ti-6Al-4V tubes (external diameter 20 mm internal diameter 10 mm) containing glass-ceramic, with a 0.008 inch (approximately 2 mm) diameter Kovar pin set in the glass-ceramic; a schematic diagram is shown in Figure 3.1. Both the Ti-6Al-4V and Kovar were supplied by Testbourne Ltd. Some Kovar pins were also used in experiments to examine the oxide layer following pre-oxidation, this Kovar was again supplied by Testbourne. The Kovar wire was in the as-drawn, not annealed, state. The Ti-6Al-4V tubes were made by drilling out the centre of an extruded rod, and machining the inner surface to achieve a consistent finish, and to bevel the internal edges.

Prior to assembly the metal components and preforms were ultrasonically cleaned in solvents in accordance with the standard procedure given by Donald [25]:

1. Ultrasonicate in dichloromethane for 2 minutes (repeated twice).
2. Ultrasonicate in detergent solution for 2 minutes.
3. Rinse under tap water.
3.2. Seal components and methods of manufacture

4. Ultrasonicate clean in de-ionised water for 2 minutes.

5. Ultrasonicate in isopropanol for 2 minutes.

6. Leave to dry on a lint-free cloth.

The detergent solution consisted of isopropanol (2400 ml), de-ionised water (600 ml), triton N101 (6 ml) and SPAN 80 (0.5 ml). Excess solvent or detergent was shaken off between stages.

The Kovar pins were then pre-oxidised, as discussed in Section 3.3, prior to assembling the seals.

![Figure 3.1: Schematic diagram of the seal design used for this project.](image)

3.2.2 Glass and glass-ceramic production

The glass was prepared from oxide and carbonate powders, as detailed in Table 3.1, to give a glass with nominal composition given in Table 3.2. The powders were dried and then mixed by rolling in a bottle on a Capco Model 12 mill for 12
Chapter 3. Seal manufacture and characterisation methods

hours. Half the powder mixture was heated in a platinum crucible, in a Carbolite BLF-1700 furnace, for four hours at 1000 °C to allow it to calcine. It was then heated to 1400 °C and held for a further four hours to melt the glass and then removed from the furnace, after which the remaining powder was added. The mixture was then heated for a further 12 hours at 1200 °C. The molten glass was quenched into demineralised water. The frit produced was dried and remelted at 1400 °C for four hours in a platinum crucible. Expansion bars, used for measuring the thermal expansion of the glass, were prepared in preheated moulds, and annealed at $T_g$, whilst the rest of the glass was quenched into demineralised water. Initially, samples were made by packing ground glass into the titanium housing and around the pin. This resulted in a large degree of porosity and variation between seals that were nominally the same. A typical micrograph is shown in Figure 3.2. As a result it was decided to change to using pressed powder preforms.

Figure 3.2: Typical back scattered electron micrograph of a seal made with pressed powder. Note the high degree of porosity.
3.2. Seal components and methods of manufacture

Table 3.1: The reagents used to manufacture the SRBAL glass.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Supplier</th>
<th>Purity(%)</th>
<th>Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strontium carbonate (SrCO$_3$)</td>
<td>Sigma Aldrich</td>
<td>≥99.9</td>
<td>60.63</td>
</tr>
<tr>
<td>Boron oxide (B$_2$O$_3$)</td>
<td>Arcos Organics</td>
<td>98</td>
<td>25.41</td>
</tr>
<tr>
<td>Aluminium oxide (Al$_2$O$_3$)</td>
<td>Sigma Aldrich</td>
<td>99.8</td>
<td>13.96</td>
</tr>
</tbody>
</table>

Table 3.2: Nominal molar composition of SRBAL glass.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Composition (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrO</td>
<td>45</td>
</tr>
<tr>
<td>B$_2$O$_3$</td>
<td>40</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>15</td>
</tr>
</tbody>
</table>

3.2.3 Preform manufacture and properties

To make preforms, the glass was prepared in the same way as before. Initially it was annealed in graphite moulds prior to processing but this produced a glass that was too hard so the glass was re melted and quenched in deionised water before being processed into pressed powder preforms by Mansol Preforms Ltd. The glass was ground in an alumina crucible until the particles were less than 75 µm diameter and the glass powder was mixed with water and a polymer binder. The mixture was pressed in a die and a two-stage heating process was used to burn out the binder and partially sinter the glass particles. The preforms were sized so that they slid in to the titanium rings and over the Kovar wire, demonstrated schematically in Figure 3.3. Preforms were (7.0 ± 0.1) mm tall with (9.90 ± 0.05) mm diameter and central hole of (2.1 ± 0.05) mm diameter.

The preforms had some porosity, a fraction of which persisted in the seals made with them. The volume fraction and pore size were, however, more consistent than when loose powder was used and there were no large pores that would effect the structural integrity of the seals. A representative micrograph of a preform is shown in Figure 3.4, and a micrograph of a seal made with a preform is shown in
Figure 3.5. Unexpectedly, the preforms contained lead, revealed by EDX analysis. There were only small amounts of lead, thought to be a result of contamination during manufacture. The contamination is isolated to small areas and is not expected to impact the seal quality or to effect the reactions between glass and metal in uncontaminated areas. Some examples are shown in Figure 3.6.

Altering the heat treatment used to make the seal, discussed in Section 3.3, alters the CTE of the glass-ceramic. CTE data for a range of heat treatments is shown in Figure 3.7 and Table 3.3. By choosing a specific heat treatment the CTE of the glass-ceramic can be tailored to be between that of the titanium and Kovar, as seen in Figure 3.7. X-ray diffraction (XRD) studies\(^2\) showed that the glass-ceramic contained two crystal phases; strontium dialuminium diborate \(\text{SrAl}_2\text{(B}_2\text{O}_7)\) and strontium metaborate \(\text{SrB}_2\text{O}_4\).

Figure 3.3: Schematic showing how the seal components slide inside one another. Titanium ring (bottom), pressed powder preform (middle) and Kovar wire (top).

Although the focus of the work was on the interfaces of the seals, a micrograph of the bulk of the SRBAL glass-ceramic in a seal made with a pressed powder preform is shown in Figure 3.8 so that it is familiar when seen later in the context of the interfaces. The crystals are visible, the darker phase, surrounded by glassy phase, the lighter phase.

\(^2\)XRD performed by Martyn Staff
3.2. **Seal components and methods of manufacture**

Figure 3.4: Back scattered electron image of a polished cross section through a pressed glass powder preform.

Figure 3.5: Typical back scattered electron micrograph of a seal made with a preform. Note the reduced porosity compared with the pressed powder sample.
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Figure 3.6: An area of the a preform containing lead. The spot labelled "1" contained approximately 5 at.% lead, as measured by EDX.

Figure 3.7: CTE data for SRBAL treated at different temperatures as compared to CTE data for Ti-6Al-4V and Kovar alloys. Data collected by Martyn Staff.
Table 3.3: Coefficients of thermal expansion for the seal components. Note that changing the sealing temperature affects the CTE of the glass-ceramic and therefore this has to be tailored to give a suitable stress state. Data collected by Martyn Staff, except that for Ti-6Al-4V which was obtained from literature [117].

<table>
<thead>
<tr>
<th>Material</th>
<th>CTE $\times 10^{-6}$ °C</th>
<th>Temperature range / °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-6Al-4V</td>
<td>9.7</td>
<td>20-650</td>
</tr>
<tr>
<td>SRBAL glass</td>
<td>6.2</td>
<td>30-420</td>
</tr>
<tr>
<td>SRBAL 750 °C 20 minutes</td>
<td>8.0</td>
<td>30-420</td>
</tr>
<tr>
<td>SRBAL 800 °C 20 minutes</td>
<td>6.5</td>
<td>30-420</td>
</tr>
<tr>
<td>SRBAL 850 °C 20 minutes</td>
<td>5.7</td>
<td>30-420</td>
</tr>
</tbody>
</table>

Figure 3.8: Typical electron micrograph of the SRBAL glass-ceramic in a seal.
3.2.4 Component assembly

A graphite jig was used to hold the components in place during assembly and sealing. The titanium ring was placed on the jig, with the pin held vertically in the centre and the glass preform was slid over the pin. A cylindrical weight of approximately 14 g and 10 mm diameter was placed on the top of the glass, separated by a graphite spacer, in order to improve densification of the glass and stop a large meniscus forming. A schematic diagram is shown in Figure 3.9. The assembly was then placed in an oven to soften the glass and form a seal.

Figure 3.9: A schematic cross sectional diagram of the components assembled on the graphite jig ready to undergo a sealing cycle.

3.3 Heat treatments

The Kovar wires were pre oxidised in air at either 700°C or 800°C for ten minutes or 800°C for 17 minutes. Further information on the pre oxidation is given in Chapter 4.
The heating schedule used to make the seals varied slightly from the traditional treatment by omitting the nucleation stage as SRBAL glass crystallises from the surface. The heat treatment was defined on the basis of CTE data from dilatometer bars and the results of hermeticity tests of seals produced using different schedules. Altering the heat treatment alters the CTE of the glass-ceramic and thus the stress within the seal, as discussed in Chapter 2. The seals were treated in a Camco G-1600 furnace in an argon atmosphere. The furnace was pumped down to a vacuum of $10^{-3}$ mbar and then filled with argon for three further pump down cycles to give a high purity argon environment. The seals were heated at a rate of 20 °C per minute from room temperature up to 600 °C then at 10 °C per minute to 800 °C where they were held for 20 minutes. They were then cooled to 500 °C at 5 °C per minute and then back to room temperature at 2 °C per minute. The treatment is shown schematically in Figure 3.10.

Some samples were made using different schedules in an attempt to alter the interfacial layers. For example, a hold at 800 °C for 60 minutes rather than the normal 20 minutes was used. The seals, however, were still heated to, and cooled from, 800 °C at the same rates.

The convention adopted in this thesis is to define sealing time and temperature by the hold time at the maximum temperature. An example of a frequently used sealing cycle is shown in Figure 3.10.
3.4 Quality control of seal manufacture

3.4.1 Hermeticity

The primary means for assessing seal quality was hermeticity, as measured by a standard helium leak test. Seals were considered to have passed the leak test if they had leak rates of $10^{-9}$ mbar l s$^{-1}$ or less, with the equipment used a leak rate of below $10^{-9}$ mbar l s$^{-1}$ could not be measured.\footnote{Leak tests were carried out by Martyn Staff}

3.4.2 Cracking along interfaces and in glass-ceramic

In addition to the quantitative pass / fail of the leak test, the quality of the seal was also assessed by the presence or absence of cracking in cross-sections.
prepared for microscopy, the process of which is outlined in Section 3.5. Early seals without pre-oxidised pins had cracking all around the pins, causing them to leak, and many seals have had cracking in the glass-ceramic and along the glass-ceramic to titanium interface as well, indicating an unsatisfactory stress state and poor quality seal.

3.4.3 Porosity in the glass-ceramic

All of the seals made for this project had some degree of porosity in the glass-ceramic. Initially, with the pressed powder seals, there was enough porosity to create structural problems and there were large voids, frequently over 1 mm across, in some samples. As manufacturing processes improved the porosity ceased to be a structural problem but was still present and large numbers of pores were visible in cross-sections of seals. Although they were smaller and more evenly distributed in the seals made with preforms, they were more numerous. The porosity does not prevent the production of hermetic seals but was still a potential concern. The porosity for a number of seals was measured to determine whether it was a result of incomplete densification of the preforms or from deleterious reactions occurring during the sealing process.

Seals were sectioned and polished, as described in Section 3.5, and backscattered electron images were collected, as they provided clearer contrast of the pores compared with secondary electron images, at 100× magnification in a cross pattern centred on the pin as shown in Figure 3.11. The polishing regime, working distance in the microscope, contrast and brightness were all kept the same so as to minimise spurious variation of porosity quantification.

The images were analysed with the ImageJ software package. The images were smoothed (10 times) and thresholded before using the Analyse Particles function.
Chapter 3. Seal manufacture and characterisation methods

Pores smaller than 10 pixels and with circularity lower than 0.5 were discarded to reduce the number of erroneous artefacts picked up. The threshold level was chosen by eye for each image. As many of the shallower pores were in shadow on one side and illuminated more on the other, only a section of the pore was analysed. To overcome this, the pores were manually outlined prior to running the counting algorithm.

Outlines of the counted pores, created by ImageJ, were manually compared with the original image to confirm that the count was accurate for all of the initial analyses. Occasional checks were made during the rest of the analyses and no noticeable errors were detected.

The preforms had a porosity of \((8.7 \pm 0.7)\%\) and the seals made from preforms had a porosity of \((8.4 \pm 0.2)\%\). Since there is no significant difference between the two results, this indicates that the porosity in the seals is most likely from incomplete densification rather than the result of any evolution of gasses during the sealing cycle.
3.4.4 Pin pull testing

Pin pull testing was performed by Martyn Staff in order to give some quantitative measure of seal quality, to determine if changing the pre-oxidation of Kovar could improve seal strength and to give a fracture surface to assess if the glass-ceramic had bonded to the pin at all. The seals were held in a jig and the pins pulled out using an Instron tension testing machine. Both 700 °C and 800 °C oxidation resulted in similar strengths and similar fracture surfaces.

3.5 Sample preparation

3.5.1 Cutting, grinding and polishing

Seals were sectioned either vertically or horizontally with a SiC blade using an Accutom 5 precision cutter. 1 mm thick sections were cut using the same method for sample preparation for thin foil electron microscopy.

Samples to be polished were mounted in Struers EpoFix, or Levocit if edge retention was important. Seals were then polished according to the procedure shown in Table 3.4 and other samples were polished using a Struers Planopol with a range of SiC grinding papers and fixed pads depending on the sample. The typical polishing regime was to use 600 grit SiC papers until the samples were planar then go through the grit sizes to 4000 grit, followed by a 3 μm diamond polish and then 1 μm diamond or 0.04 μm colloidal silica suspension (OPS). Some small alterations to the times used were made depending on the characteristics of the sample. The OPS solution etches the samples slightly, revealing some grain structure in both titanium and Kovar but also etching the glass away more than
the crystals in the glass-ceramic so was not used for most seal samples unless showing grain structure in the metal samples was desirable.

Table 3.4: The standard grinding and polishing procedure used for cross sectioned seals.

<table>
<thead>
<tr>
<th>Paper / pad</th>
<th>Force</th>
<th>Time (minutes)</th>
<th>Speed (rpm)</th>
<th>Lubricant</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC 600</td>
<td>3</td>
<td>Until planar</td>
<td>150</td>
<td>Water</td>
</tr>
<tr>
<td>SiC 800</td>
<td>3</td>
<td>2:00</td>
<td>150</td>
<td>Water</td>
</tr>
<tr>
<td>SiC 1200</td>
<td>3</td>
<td>1:30</td>
<td>150</td>
<td>Water</td>
</tr>
<tr>
<td>SiC 2500</td>
<td>3</td>
<td>1:30</td>
<td>150</td>
<td>Water</td>
</tr>
<tr>
<td>SiC 4000</td>
<td>3</td>
<td>1:30</td>
<td>150</td>
<td>Water</td>
</tr>
<tr>
<td>Dac 3 µm</td>
<td>3</td>
<td>4:00</td>
<td>150</td>
<td>DP Blue</td>
</tr>
<tr>
<td>Dac 1 µm</td>
<td>3</td>
<td>2:00</td>
<td>150</td>
<td>DP Blue</td>
</tr>
</tbody>
</table>

3.5.2 Coating

Non-conducting samples were coated prior to analysis in the scanning electron microscope, using either ∼2 nm of gold, deposited with a Emitech K575X sputter coater, or a carbon layer deposited with an Edwards Auto 306 thermal evaporator. Samples for focussed ion beam (FIB) milling were coated with ∼15 nm of gold so that the gold layer could withstand more beam damage from the ion beam. All seal cross-sections were coated; without coating it was not possible to perform electron microscopy of the interfaces because of the insulating glass, particularly at the pin / glass-ceramic interface as the pins were isolated from ground by the surrounding glass-ceramic and mounting resin.

3.5.3 Focussed ion beam (FIB) milling

Thin foils for use in scanning transmission electron microscopy (STEM) were prepared using an FEI Nova Nanolab dual beam FIB. Ion milling was carried
out using a gallium source and a platinum strap was deposited to protect foils during milling. Foils were attached to Ominiprobe copper TEM Lift-Out grids using platinum or tungsten deposition. Standard lift out techniques were used. Final polishing was carried out at 100 pA beam current.

3.6 Analysis methods

3.6.1 Scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDX) and wavelength dispersive x-ray spectroscopy (WDS)

SEM was performed using a JEOL 7100-F with a Schottky field emission electron gun and fitted with Thermo Scientific UltraDry EDX detector (a silicon drift detector with 30 mm$^2$ collection area), Thermo Scientific Magnaray WDX detector and NORAN System 7 X-ray Microanalysis System. Back scattered electron micrographs were collected with a solid state detector. Typically a beam potential of 15 kV was used for secondary electron and backscattered electron imaging as well as EDX collection since all of the elements expected to be in the samples have peak energies that can easily be excited by a 15 keV beam energy (Sr, Fe, Co and Ni all have peaks in the range 4-8 keV). Beam current was generally around 2 - 4 nA for imaging.

When collecting WDX spectra and maps, a beam current of around 27 nA was used to provide a higher count rate, and collection times were typically 60 - 120 minutes for each element map. Both EDX and WDS maps were collected as EDX allows parallel acquisition of all energies, and all analysable elements, so maps of every element of interest can be collected from the same area at the same time.
In contrast, WDX analysis can only be performed on one wavelength at a time unless multiple detectors are used, therefore WDX maps must be collected in series. This extends acquisition time and creates the potential for the acquisition areas to be different from one element map to the next as a result of drift. EDX maps can also be used for principal component analysis, which was performed using Thermo Scientific’s COMPASS software.

### 3.6.2 Scanning transmission electron microscopy (STEM)

STEM was performed using a Hitachi HD-2300A ultra-thin film evaluation system, a dedicated STEM. All analyses were carried out using a 200 kV beam. EDX data were collected with an EDAX silicon drift detector with a collection area of 10 mm$^2$. Electron energy loss spectroscopy (EELS) data were collected with a Gatan Enfina 776 electron energy loss spectrometer. Images were collected and analysed with Gatan’s DigitalMicrograph software.

### 3.6.3 X-ray photoelectron spectroscopy (XPS)

XPS was performed using a Thermo Scientific Theta Probe spectrometer with a monochromated Al Kα X-ray source ($h\nu = 1486.68$ eV). Survey spectra were acquired using a 300 eV pass energy and high resolution spectra were collected with a 50 eV pass energy. Energy step sizes of 0.5 and 0.1 eV for survey and high resolution spectra respectively. An analysis time of 50 ms was used for all spectra. All spectra were charge corrected to the C 1s photoelectron peak at 285.0 eV. Data were processed with the Avantage v5.926 software package.
3.6.4 X-ray diffraction (XRD)

Both glancing angle and powder XRD were carried out using a PANalytical XPert Pro X-ray diffractometer. Copper Kα radiation was used, with a wavelength of 1.540598 Å. A 2θ range of 15 - 75 ° was used with a step size of 0.1 °.

3.6.5 Raman spectroscopy

Raman spectroscopy performed using a Renishaw Systems 2000 Raman Microscope equipped with a 20 mW 514 nm argon-ion laser. The operating power was reduced by 50 % in order to reduce the chance of sample damage. Spectra were collected using the Renishaw WiRE software and analysed with Galactic GRAMS/32 software.
Chapter 4

The titanium to SRBAL glass-ceramic interface

4.1 Introduction

There is some evidence in the literature that titanium borides may form at the interface between titanium and boroaluminate glasses during sealing or heating [8] [6] [89]. There is not, however, an extensive body of work and much of it focusses on model systems and systems heated for greatly increased times in order to make interpretation easier. Additionally, there is a wide range of boroaluminate glasses and only a tiny number have been characterised fully. It is important to characterise the specific system used in this work to determine if borides are formed with this glass, which also contains strontium, and at the shorter heating times used in practical seal production. Since boroaluminate glasses have been chosen specifically because the reactions between the glass and titanium alloys are slow, it is quite possible that the reaction products (if they exist) will only be found in small amounts.
4.2 Scanning electron microscopy of the interface

4.2.1 Introduction

All of the seals produced for investigation in this project were cross-sectioned and metallographically polished (as described in Chapter 3) as part of the initial characterisation and quality check. Polished sections were also used for analysis of the Kovar to SRBAL interface and reactions. Although it was not expected that the interfacial reaction products would be produced in sufficient quantities to be observable or detectable simply from electron microscopy and the X-ray spectroscopy of cross sections, SEM, EDS and WDS analysis was performed.

4.2.2 Imaging of polished cross-sections

Examples of the typical structures and features observed in the metal to glass-ceramic interface region are shown in the electron micrographs of the interface in Figures 4.1, 4.2, 4.3 and 4.4. They show that the only observable effect on the microstructure of the glass-ceramic is an increase in porosity in some areas. No other changes are observable over a distance that can be studied using SEM of cross-sections. No interfacial reaction products / layers are observable at the interface and the crystallisation of the glass-ceramic is not altered in the interface region. In areas, such as that shown in Figure 4.2, where porosity in the glass-ceramic is increased near to the interface with the titanium, this is thought to be the result of contamination on the components, as was discussed in Section 2.1.5. The crystals in the glass-ceramic can also bee seen in the micrographs in Figures 4.3 and 4.4, as the darker phase.
4.2. Scanning electron microscopy of the interface

Figure 4.1: Back scattered electron micrographs of cross-sectioned seals. The titanium housing is shown on the left hand side of the micrograph part a, and the right hand side of part b, the glass-ceramic is on the right and left respectively. Porosity in the glass-ceramic is clearly visible.

Figure 4.2: Back scattered electron micrograph of a cross-sectioned seal. The titanium housing is shown on the left of the micrograph, and the glass-ceramic on the right. Porosity is increased near the interface.

In some micrographs, such as Figure 4.4, there is a brighter region along the interface, which could be taken as some evidence of interfacial reaction. However, any possible layers that may exist can easily be hidden within edge effects generated
Chapter 4. The titanium to SRBAL glass-ceramic interface

Figure 4.3: a) Secondary and b) backscattered electron micrographs, each of the same area of the titanium to glass-ceramic interface. Grain structure is visible in the titanium as a result of polishing with colloidal silica. Crystals can be seen in the glass-ceramic.

by the change in height of the sample at the interface (the glass-ceramic polishes at a faster rate than the titanium, so there is a small step at the interface). The glass-ceramic has lower density than the titanium and has significantly lower X-ray and electron attenuation coefficients than the titanium housing. As a result of this X-rays and backscattered electrons that are produced from the titanium are able to escape through the glass-ceramic, generating a larger secondary electron cascade, producing a bright band. This is a more likely explanation for the brighter region that can be seen in some electron micrographs of the titanium to SRBAL interface than the presence of an interfacial zone. However, if there is in fact a layer then it cannot be accurately identified since the aforementioned edge effects will interfere with interpretation. Some samples were made with increased sealing times (the longest being a hold time of 240 minutes at 800 °C) and the same features, or lack thereof, were seen.

In some samples, but not all, there is a zone near to the interface where the porosity in the glass-ceramic is increased (both the number of pores is increased and their average size). Even samples with an increased degree of porosity were found
4.2. Scanning electron microscopy of the interface

Figure 4.4: Higher magnification electron micrograph of the SRBAL (left) to titanium (right) interface. The crystals in the glass-ceramic grow uninterrupted up to the titanium and there is no obvious sign of any interfacial reaction zone. The brighter edge to the titanium may be a result of some compositional change but may also be the result of edge effects resulting from the titanium polishing slower than the glass-ceramic or a work hardened layer (discussed in Section 4.5).

to be hermetic (assuming they were made under the correct sealing conditions) as there is not enough porosity to create a path through the seal from one side to the other. The porosity is believed to be the result of organic contamination on the components (either the titanium rings or the glass-ceramic preforms). When the samples are heated during production of the seal the organic material could degrade, resulting in evolution of gasses during sealing. This is a known cause of porosity in glass-to-metal seals [25].
4.3 Wavelength dispersive X-ray spectroscopy of polished cross sections

Since boron is difficult to detect with EDX, because of its low atomic number, the EDX analysis at the interface was complemented by acquiring WDX data for boron. X-ray maps of the interface are shown in Figure 4.6 and a line scan is shown in Figure 4.5. Each of the maps was processed using net counts to minimise the effect of the background. A clear increase of boron is seen at the interface. This was observed in multiple samples, at numerous sites and at different orientations and take off angles, removing the possibility of an edge effect. This is consistent with the hypothesis, based on the literature discussed in 2.3.2, that a titanium boride layer is formed at the interface. Similar observations were made for seals produced in sealing runs for 240 and 60 minutes at 800 °C as well, the layer appeared to be similar thickness (though the spatial resolution of the WDS maps is limited).

Figure 4.5: WDX line scan for boron across the interface from a glassy region in the SRBAL glass-ceramic (left) to titanium (right). There is a sharp increase in the boron signal at the interface. The same boron peak is seen at the interface between a crystals in the glass-ceramic and the titanium.
Line scans across the interface show the same boron increase as is observed in the X-ray maps. Additionally, a corresponding decrease in the aluminium intensity is observed at the interface. This again supports the expectation that there will be a titanium boride at the interface (which would not contain aluminium).

Figure 4.6: EDX and WDX (boron only) maps of the titanium to SRBAL interface in a sample that underwent the standard 800°C for 20 minutes sealing cycle. There is a clear increase in the boron WDX signal near to the interface, seen as a bright line in the boron WDS map (marked by an arrow to the right of the boron).
4.4 Fracture samples: characterisation of the boride layer

4.4.1 Sample production

It was deemed likely that an interfacial layer of titanium boride formed during seal manufacture. If such a layer has been created then one way to confirm its presence would be to look for it in a fracture surface, as this layer may remain adhered to one side of the interface. In order to investigate this samples were made that could be fractured and either side of the fracture surface analysed.

Cuboids of approximately 1 × 1 mm cross-section were cut from the seals so that one half was glass-ceramic and the other was titanium, as shown schematically in Figure 4.7. Samples were fractured by striking the area of the interface with a small hammer, this was performed in air because of the difficulty of producing samples that could be fractured in a fracture stage attached to a ultra high vacuum instrument. Without scoring or otherwise trying to control where the samples failed they frequently failed either at or near the interface, often with some areas of the metal appearing to have no glass-ceramic adhered and other areas with a thin covering of a few 100 µm. Some samples failed one to two millimetres into the glass but were not used for this analysis. Representative micrographs of fracture surfaces are shown in Figures 4.8, 4.9 and 4.10.

Figure 4.7: Schematic of the samples cut for fracturing.
4.4.2 Imaging

The samples described in Section 4.4.1 were imaged before further characterisation was performed. It appeared to the naked eye that there were areas of the titanium with no glass adhering, a closer investigation with SEM showed that there was in fact a layer on the titanium. When these areas were imaged it was clear that at the edge of the glass patches there was no defined end to the glass but instead it merged into a thin layer that covered the titanium. When imaging the layer, some slight charging occurred, indicating that an insulating layer was present on the titanium, but the level of charging was much less than was seen on the thick glass regions (where the glass was much thicker than the electron beam depth).

The two regions, with either a thick glass-ceramic coating (of 100 µm or more) or a thin coating (that is thin enough to image the titanium through) give two areas that represent the glass-ceramic in the bulk and at the interface respectively, micrographs showing surfaces that have both thick glass-ceramic on some areas and the thin coating on others are shown in Figures 4.8 and 4.9. These two types of area were used to study the interface using spectroscopic techniques.

4.4.3 Wavelength dispersive x-ray spectroscopy

Previous studies of the fracture surfaces of titanium to aluminoborate glass seals have found that, on the titanium side of the failed seal, boron was present in both borate and boride states [8]. The boride was believed to be the phase adhered to the titanium.

As there were only small areas that fractured near to the interface in the samples investigated here it was decided to use low energy WDX to look for the
Figure 4.8: Secondary electron micrograph of the fracture surface of the titanium to SRBAL glass-ceramic interface. On the left of the sample there is a thick layer of glass-ceramic, on the right there appears to be no glass-ceramic and the titanium is visible.

borate / boride peak shift [4], since WDX has a much greater spatial resolution than XPS, and is also capable of high enough spectral resolution, 0.2 eV. A beam energy of 5 keV and a sample current of 4 nA was used with a NiC80 diffractor crystal for the analysis. This provided a sufficiently high count rate for the B Kα peak. EDX and WDX were also used to investigate the elemental composition of the thin layer of material. EDX and WDX confirm that boron, strontium and oxygen are present on all of the areas of both thick and thin glass. Aluminium is also present (although it would be expected to be present in the glass, it is also present in the titanium as it is Ti-6Al-4V). The glass layer is thin enough that, although it charges slightly, charging does not prevent imaging or spectroscopy. Figure 4.10 shows a site used to collect WDX spectra from the thin glass region.
4.4. Fracture samples: characterisation of the boride layer

Figure 4.9: A secondary electron micrograph of a fractured titanium - SRBAL interface. Most of the surface is covered in a layer of glass tens to hundreds of microns thick, but along the top of the surface there is an area where little, or no, glass has adhered.

Figure 4.10: A secondary electron micrograph of a fractured titanium - SRBAL interface. The white box shows an area of thin glass selected for WDX analysis.
The boron peak positions were compared with spectra from TiB<sub>2</sub> powder (particle size <10 µm) purchased from Sigma Aldrich since it was expected that a titanium boride will have formed at the interface.

As can be seen in Figure 4.11, there is a measurable shift in the position of the boron peak acquired from areas of thick glass-ceramic, considered to represent the bulk glass-ceramic away from interface, and the thin glass, considered to represent the interfacial zone. The peak is shifted from 182 eV in the glass-ceramic to 184 eV in the interface material. These peaks are in agreement with the peak positions measured for a piece of glass-ceramic taken from the bulk of the glass-ceramic in a seal (182 eV) and the energy recorded for boron in the TiB<sub>2</sub> standard (184 eV). All of the analyses were carried out back to back with the same operating conditions.

Figure 4.11: Normalised and smoothed WDS spectra from glass adhered to the titanium in fracture samples and the thin layer that is bonded to the titanium. Spectra from bulk SRBAL glass-ceramic and titanium diboride shown for reference.
It should be noted that when performing WDX on crystals of TiB and TiB$_2$ there is an effect from the crystal orientation relative to the diffracting crystal which can alter both peak intensity and position [4]. However, in the work presented here, large, 100 $\mu$m$^2$ or bigger, areas which would not be expected to be single crystals and several reference spectra were collected from different TiB$_2$ particles, all of which showed consistent peak positions within the uncertainty of the signal to noise ratio. This indicates that there are borides formed at the interface between the SRBAL glass-ceramic and titanium.

4.5 Scanning transmission electron microscopy of the interface

4.5.1 Imaging and EDX

From the initial imaging of foils made from seals produced in a 800 °C, 20 minute, sealing run it was clear that there were no large interfacial reaction zones greater than 1 $\mu$m wide. Representative micrographs are shown in Figures 4.12 and 4.13.

Grains are visible in the titanium from 1 $\mu$m away from the interface, as expected. In the glass-ceramic the crystals are visible; these were confirmed to be crystalline by observing live diffraction patterns (not indexed). Dendrites extending in to the glass may have been expected, based on the work by [6], but none were visible at this scale. This may be because the sealing time was much less than used in that work and may not be long enough to enable the growth of dendrites.

There is a region of around 0.5 $\mu$m near to the interface where the structure of the titanium is altered and appears to contain needle like structures as well as having different contrast in transmission and Z contrast modes. This region is
visible in Figures 4.12 and 4.13 but is even more evident in Figures 4.14, and 4.19 (shown later).

EDX indicates that the interfacial region of the titanium alloy is depleted in aluminium compared with the bulk. The spatial resolution of EDX in thin foil microscopy is high, since the interaction volume is small. Obtaining accurate quantified information from the EDX data is problematic because there is significant background intensity caused by fluorescence of copper and titanium, from the sample holder and lift out grids. Relative amounts can, however, be compared and an example is shown in Figure 4.15 which shows a line scan across the interface.

This layer with altered composition is believed to be a result of surface work hardening of the titanium during production of the component, rather than a result of reactions with the glass-ceramic. The titanium housing rings are pro-
4.5. Scanning transmission electron microscopy of the interface

Produced by drilling out the centre of titanium rod and CNC machining the surface to achieve a consistent finish. Neither EDX or EELS show evidence of strontium or boron having diffused into the metal at this length scale.

In order to confirm that the layer in the titanium was indeed due to damage, a foil was made from a titanium ring that had been put through the same heat treatment as seals, but without the other components of the seal (so it was not in contact with any glass). This foil also had a layer of approximately 0.5 µm along the machined surface where the microstructure had been altered. Representative micrographs are shown in Figures 4.16 and 4.17. The damaged layer also had a different composition, with EDX showing that it contained much less aluminium than the titanium just 250 nm into the ring. The aluminium is under counted in both cases due to the mixture of copper and titanium background signals that are
Chapter 4. The titanium to SRBAL glass-ceramic interface

Figure 4.14: Transmission mode micrograph of the titanium to SRBAL (same foil as in Figure 4.12). Titanium on the left, SRBAL on the right. Some beam damage is visible on the glass-ceramic.

Figure 4.15: EDX line scan across the titanium (left) to SRBAL (right) interface. Neither titanium or vanadium appear to have diffused into the glassy region of the glass-ceramic any further than 0.1 µm. The region of titanium alloy near to the interface appears to be depleted in aluminium and titanium and enriched in vanadium. Boron is not included as it cannot be detected with any degree of accuracy.
unavoidable. Additionally, vanadium is poorly counted in EDX analysis because the V Kα peak overlaps with the Ti Kβ peak. As a consequence of the much greater concentration of titanium (90 wt. %) compared with vanadium (4 wt. %) the V Kα peak is lost in the intense Ti Kβ peak. Figure 4.18 shows sites used for EDX analysis of this damaged layer.

![Image of a transmission electron micrograph of a foil made from a heated titanium ring. The damaged layer is indicated with an arrow and dotted lines either side.](image)

**Figure 4.16:** Transmission electron micrograph of the foil made from a heated titanium ring. The damaged layer is indicated with an arrow and dotted lines either side.

In Section 4.2.2 it was observed that there is sometimes a brighter region in the titanium (in back scattered imaging) when cross sections of seals are imaged. This was believed to be an edge effect. An alternative explanation is that the observed layer is the damage layer that is seen in the foils analysed with STEM. The layer appears dark in bright field imaging (indicating a higher atomic number than the bulk), and appears bright in backscattered electron imaging (again indicating a high atomic number). Decreased aluminium content (atomic mass 27) and increased titanium content (atomic mass 48) could explain the contrast difference.
Chapter 4. The titanium to SRBAL glass-ceramic interface

Figure 4.17: Transmission electron micrograph of the foil made from a heated titanium ring.

<table>
<thead>
<tr>
<th>Site 1 (left)</th>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Aluminium</td>
<td>4.3 (4.6)</td>
<td>7.5 (7.9)</td>
</tr>
<tr>
<td></td>
<td>Titanium</td>
<td>89.2 (95.4)</td>
<td>87.7 (92.1)</td>
</tr>
<tr>
<td></td>
<td>Copper</td>
<td>6.5</td>
<td>4.8</td>
</tr>
<tr>
<td>Site 2 (right)</td>
<td>Aluminium</td>
<td>0.4 (0.4)</td>
<td>0.7 (0.7)</td>
</tr>
<tr>
<td></td>
<td>Titanium</td>
<td>93.1 (99.6)</td>
<td>94.3 (99.3)</td>
</tr>
<tr>
<td></td>
<td>Copper</td>
<td>6.5</td>
<td>5</td>
</tr>
</tbody>
</table>

Figure 4.18: The site of EDX analysis on the titanium foil, site one is in the bulk and site two site is on the damaged surface layer. EDX quantification data are given in the table below (values in brackets are with the copper removed).
4.5. Scanning transmission electron microscopy of the interface

Figure 4.19: Transmission mode micrograph of the titanium to SRBAL (same foil as in Figure 4.14. Titanium on the left, SRBAL on the right.

4.5.2 Electron energy loss spectroscopy

Electron energy loss spectroscopy (EELS) can be used to detect boron, oxygen and titanium. However, EELS cannot be used to analyse aluminium and strontium. Aluminium has L2 and L3 lines starting at 73 eV but they have a poorly defined shape and are not a desirable peak to analyse. The aluminium K peak at 1560 eV is more well defined but, since it is at high energy, the beam would need to be much more intense in order to produce a usable signal. The strontium L3 and L2 peaks are at 1940 eV and 2007 eV respectively. The use of a beam with sufficient intensity to analyse these lines would cause too great a degree of beam damage in the glass.

EELS point analyses of the glassy phase of the glass-ceramic 150 - 200 nm away from the interface show no signal from titanium, indicating that titanium has not diffused in to the glass over distances of this order. Point analyses were also
performed in the titanium 150 - 200 nm away from the interface, and no boron
was detectable, indicating that boron has not diffused in to the titanium over
these length scales. It is possible that with a thinner foil, and correspondingly
improved signal to noise ratio, that the detection limit would be lowered and
titanium may be detected in the glass, and boron in the titanium, but with
the samples available there is no evidence of this. Increasing acquisition time
is problematic as the beam rapidly damages the glass. Line scans are shown
in Figures 4.20 and 4.21 for boron, titanium and oxygen. They show that the
interface layer contains a higher concentration of boron than the surrounding
glass, and that the boron does not extend more than a few tens of nanometres in
to the titanium. The titanium signal rapidly drops to zero (when noise is taken
into account) once past the observable interface region that is around 40 nm wide
in Figure 4.20. The oxygen signal is much lower in the interface region than in
the glass, and sometimes drops to zero. Considering the titanium, boron, and
oxygen signals together indicates that there is a layer at the interface that is rich
in boron and titanium, but poor in oxygen. This again supports the hypothesis
that titanium boride has formed at the interface during sealing. It should be
noted that the alignment of the interface is not perfect, and as such the interface
will not be perpendicular to the beam. This may explain why there is some boron
signal on the titanium side of the foil, or it may also be that a small amount of
boron has diffused into the titanium.

Analysis by electron energy loss spectroscopy (EELS) shows that, at distances
of greater than 1 µm, titanium and vanadium have not diffused in to the glass-
ceramic, and that boron and strontium have not diffused in to the titanium.
4.5. Scanning transmission electron microscopy of the interface

Figure 4.20: EELS line scan across the interface from titanium (left) to SRBAL glass-ceramic (right). There is no titanium found outside of the interface zone, indicated by the parallel dashed lines, which extends 40-50 nm into the glass-ceramic. The interface zone contains elevated levels of boron and reduced levels of oxygen. This is consistent with the hypothesis that the interface layer contains titanium boride.

Figure 4.21: EELS line scan across the interface from titanium (left) to SRBAL glass-ceramic (right). There is no titanium found outside of the interface zone which extends 40-50 nm in to the glass-ceramic. The interface zone contains elevated levels of boron and reduced levels of oxygen. This is consistent with the hypothesis that the interface layer contains titanium boride. The black circle near the bottom of the micrograph is beam damage created when aligning the beam for analysis of this area.
4.5.3 Limitations of EELS and STEM

Whilst STEM and EELS performed on foils prepared by focussed ion beam milling are excellent techniques that are well suited for studying the interface, they do have some limitations and issues when studying this specific system. Beam damage can be seen in many of the micrographs shown in this chapter. The titanium side of the foil does not show any sign of beam damage, since it is conductive and can dissipate charge, but the glass / glass-ceramic is damaged quickly, the time taken to align the beam is enough to burn all the way through the sample and line scans with dwell time of only one or two seconds per point result in visible changes. To illustrate the rate of damage, a series of 30 one second acquisitions was performed on the same site and the EELS spectra compared (see Figure 4.22). As the foils are not especially thin the peak to background ratio is low. However,

Figure 4.22: EELS spectra collected from one spot, showing the titanium L1 and L2 peaks. Spectra were collected for 1 second each. The peak to background ratio can be seen increasing as the sample is thinned by the beam damage. Spectra are off set for ease of interpretation.
initially, the beam thins the foil when it is incident on the glass-ceramic and the peak to background ratio increases as the foil thins. This shows how easily the glass is damaged. Alignment of the foils in STEM is also challenging because the interface region is not crystalline so the foil cannot be aligned on a crystalline phase.

The poor signal to noise ratio, and inability to increase acquisition time, as beam damage will alter the sample, mean that acquiring accurate quantification data from EELS is problematic. In addition, the background spectrum is defined manually for each element of interest and noise in the spectra often mean that negative quantification is given in areas of the sample that have little or none of the element being quantified. However, a broad interpretation of the relative total counts in one area of a sample compared with another, for example along a line scan, can still be performed.

Additional loss of accuracy in quantification is caused by a significant amount of carbon contamination on the surface of foils that was introduced by the FIB milling. The carbon contamination increases the background in the spectrum, which reduces the precision of the quantification.

The process of FIB milling and the impact on the foil produced also needs consideration. The glass mills more rapidly than the titanium, so the glass end of the foil ends up being thinner than the titanium end. This step change in the foil thickness introduces the possibility that material milled away during the thinning process may be redeposited in the slightly sheltered area at the thickness change. Since the glass charges it is typically preferable to attach the titanium side of the foil to the lift out grid, otherwise the platinum strap is the only conduction path to earth the glass section of the foil. However, the glass still charges sometimes during thinning which deflects both the electron and ion beam, making
an evenly thinned foil hard to produce. The sample also contains some residual stress, introduced during the seal manufacture, which is released during thinning and can cause foils to twist. These reasons all combine to increase the challenge of producing a thin and uniform foil from FIB milling.

4.6 Conclusions

Detailed in this chapter are the results from a range of analytical techniques which provide evidence that there is a titanium boride layer formed at the interface between titanium (Ti-6Al-4V) and SRBAL glass-ceramic in the samples analysed. WDS of cross sections showed an increased boron content at the interface, which was supported by EELS which also showed an increase of boron at the interface. WDS of fractured samples indicated that the boron in the interfacial zone is in the form of a boride, whereas the boron in the bulk of the glass-ceramic is in the borate state (as expected). This indicates that there is a titanium boride formed at the interface that adheres to the titanium when samples are fractured. The formation of this layer does not appear to be detrimental to seal performance.

Additionally it has been shown that in samples made under typical sealing conditions boron does not diffuse in to the titanium and titanium does not diffuse more than 50 nm in to the glass-ceramic. The titanium boride does not appear to be dendritic but instead appears amorphous. This is contrary to the work of Brow et al. [6]. However, in these studies the titanium boride dendrites were only found in seals heated for much longer durations, between 3 and 240 hours [88]. The formation of dendrites was proposed to be beneficial for seal performance, through increased mechanical keying, but since there is no evidence provide by this work that they are formed in typical seals this hypothesis is not supported by this work. It may be possible that the boride layer may be a preferential fracture
site but, even in samples held at 800 °C for 240 minutes during sealing, cracking was not observed at the titanium-glass-ceramic interface when the seals were cross-sectioned. This indicates that the bonding of this layer is not the limiting factor in seal integrity.

This work provides the first evidence obtained via STEM for interfacial boride formation and shows that titanium boride can act as bridging compound between the titanium on one side of the interface and the glass-ceramic on the other.
Chapter 5

Kovar oxide and the Kovar to glass-ceramic interface

5.1 Introduction

In the previous chapter, a significant body of evidence was shown that pointed to the presence of titanium boride formation at the SRBAL to Ti-6Al-4V interface. Additionally it has been shown that this interface is not a site for failure of seals, indicating that bonding occurs between the glass-ceramic and metal. However, the seals of interest do not only contain titanium-SRBAL interfaces. The system also contains a Kovar-SRBAL interface which must also be studied. Thus it is important to ensure that SRBAL can also be bonded hermetically to the Kovar pins. Without a successful bond at both interfaces the seal cannot be satisfactory.

This chapter begins by showing the, poor, results of seals produced without pre-oxidising the Kovar pins and then moves to discussing the pre-oxidation of Kovar. The oxide was characterised using many techniques, which are discussed. Next, the effect of the sealing cycle (heating to 800 °C in an argon atmosphere) on the
oxide is discussed as it was shown to alter the oxide layer. The final section covers the characterisation of the interface between pre-oxidised Kovar and the SRBAL glass-ceramic, which is followed by conclusions for the chapter.

5.2 Initial seals

The first seals that were produced for this project were made with as-received Kovar pins, with only the native oxide present on the surface. As discussed in Chapter 2 it is widely accepted that the best seals of Kovar to glass are achieved by pre-oxidising the Kovar prior to sealing. The seals prepared without pre-oxidising the Kovar were found to be very poor quality (as compared with the later seals made with pre-oxidised Kovar). The seals without pre-oxidation were not hermetic and showed a large degree of cracking around the interface when sectioned and polished. Microscopy of some seal cross-sections and pin pull tests performed on these samples is given, so that their performance can be compared with that of the seals made with pre-oxidised Kovar, discussed in Section 5.5.

Microscopy on cross-sectioned samples showed that the interface between the glass-ceramic and the pin was cracked, and the bonding was so poor that the pin could sometimes be pushed out of the sample by hand once one side of the titanium housing had been cut off (since there was no longer sufficient compression around the pin to hold it in place). A representative micrograph of the interface is shown in Figure 5.1. There was no evidence of the glass-ceramic composition or structure being altered in proximity to the Kovar pin.

Pin pull tests were performed on the Kovar pins in seals made without pre-oxidising the pins, and the pins had no residual glass left on the surface, indicating

\[\text{by Martyn Staff}\]
that the glass was not bonded to the metal. Micrographs are shown in Figure 5.2.

Figure 5.2: Two secondary electron micrographs of the pin from a seal made with a pin that had not been pre-oxidised. Pin removed from the seal during a pin pull test. There is no evidence of residual glass adhering to the pin, showing that there was no probably chemical bonding across this interface.
5.3 The Kovar oxide layer

5.3.1 Samples used and preparation of the oxide

Different recommendations are made with regards to pre-oxidation in the literature, authors report work in which varying temperatures, times and atmospheric conditions are used. The impact of the different oxidising procedures on the bond is rarely considered; generally only the thickness and adherence of the thermally grown oxide layer are considered. As such it was decided to investigate in more detail the oxides that were formed by oxidation in air at 700 °C or 800 °C for 10 minutes. The oxide was chosen for investigation as it was shown experimentally, in the parallel project, that hermetic seals could be produced with the SRBAL glass-ceramic and pre-oxidised Kovar.

Two different sets of Kovar samples were oxidised and analysed: wire samples and plate samples. The wires were the same as the wires/pins used in the seals, and were purchased from Testbourne Ltd in the as-drawn state and cut to lengths of approximately 30 mm. Kovar plates were purchased from Future Alloys in 50 × 50 × 2 mm pieces and polished to a 1 μm finish. Plate samples were used so that XRD and XPS could be performed on a flat surface in order to improve the signal to noise ratio in the spectra. All samples were cleaned in acetone and isopropyl alcohol, in an ultrasonic bath, prior to the oxidation treatments. The samples were oxidised in muffle furnaces for 10 minutes at 700 °C or 800 °C in air.

5.3.2 X-ray diffraction (XRD)

The most common method used in the literature to identify the oxide that forms on Kovar is XRD and was therefore, the first analysis technique carried out on the
5.3. The Kovar oxide layer

oxidised samples. Glancing angle XRD was only performed on the plate samples and not the wire samples as the wires were too small and rough to achieve a signal with acceptable signal to noise ratio. Powder XRD was performed on the oxide from the 800 °C oxidised wires. The oxide was scraped off the wires using a stainless steel scalpel blade. The 800 °C oxide could be removed easily but the 700 °C oxide was strongly adhering and could not be removed in sufficient quantity to perform powder XRD.

Analysis of both the 700 °C and 800 °C oxidised plates produced diffraction patterns that could be indexed to Fe$_2$O$_3$ and Fe$_3$O$_4$ using cards 00-033-0664 and 00-019-0629 respectively. Diffractograms are shown in Figure 5.3.

![XRD diffractograms from Kovar plates oxidised for ten minutes in air at either 700°C (left) or 800°C (right). The patterns can be indexed fully by a combination of Fe$_2$O$_3$ and Fe$_3$O$_4$.](image)

Figure 5.3: XRD diffractograms from Kovar plates oxidised for ten minutes in air at either 700°C (left) or 800°C (right). The patterns can be indexed fully by a combination of Fe$_2$O$_3$ and Fe$_3$O$_4$.

Powder XRD of the oxide formed at 800 °C also showed strong patterns for Fe$_2$O$_3$ and Fe$_3$O$_4$, as well as weak patterns for CoO and NiO as minor phases, as indexed by cards 01-073-0603, 01-089-0950 and 00-003-0984 respectively.

The identification of Fe$_2$O$_3$ and Fe$_3$O$_4$ is consistent with much of the literature but further complementary techniques were used to provide a greater understanding of the oxide composition.
5.3.3 X-ray photoelectron spectroscopy

XPS was carried out on both plate and wire samples. The XPS analysis showed that iron, cobalt and nickel were all present in the surface of the oxide on the plate samples, possibly contrary to the initial observations from XRD. Survey spectra from plate samples are shown in Figure 5.4, with the most intense photoelectron peaks labelled.

![Figure 5.4: XPS survey spectra for Kovar plates oxidised in air for ten minutes at either 700 °C (left) or 800 °C (right).](image)

Nickel was not detected in survey scans of the pin samples, but was detected in the plate samples oxidised at both 700 °C and 800 °C. The poorer signal to noise ratio in the spectra from pins (a result of their rough surfaces and orientation) may explain the discrepancy, since the amounts of nickel are low (only around 2 at. %). In addition, the ratio of iron to cobalt was higher in the pin samples than the plate samples. This indicates that the oxides formed on the two types of sample may have some differences.

High resolution spectra of the metal / metal oxide peaks, for the pin samples, are shown in Figure 5.5. Inspection of the iron peak region revealed that the Fe$^{3+}$ satellite was present but the Fe$^{2+}$ satellite was not. The Co$^{2+}$ and Ni$^{2+}$
satellites were also observed. Since Fe$_3$O$_4$ contains both Fe$^{2+}$ and Fe$^{3+}$ this shows that Fe$_3$O$_4$ is not present in the top layer of the oxide. The presence of Fe$_2$O$_3$, CoO, NiO are consistent with these data, as are CoFe$_2$O$_4$ and mixed (Co, Ni)$^{2+}$[Fe, Co, Ni]$^{3+}$O$_4^{2-}$ spinels, where ( ) denotes octahedral sites and [ ] denotes tetrahedral sites in the spinel. The high resolution spectra of the plate samples showed the same characteristics. These have been reported previously [59].

Within the resolution limits of the XRD set up and the signal to noise ratio in the diffraction patterns it is not possible to differentiate between Fe$_3$O$_4$ and (Co, Fe, Ni)$_3$O$_4$ spinels. It is reasonable to assume that the XRD pattern previously indexed as Fe$_3$O$_4$ may be the pattern from (Co, Fe, Ni)$_3$O$_4$. Thus, the oxide layer may to be a mixture of Fe$_2$O$_3$ and (Co, Fe, Ni)$_3$O$_4$ possibly with small amounts CoO and NiO. It is also necessary to consider that the XRD signal is from a greater depth than the XPS signal and this could account for some of the differences, since there is a detection limit and if only a small amount of a phase exists on the surface it may be below the detection limit when a greater volume is analyzed.

![Figure 5.5: XPS high resolution spectra of the Fe$^{2p}$ region, performed on Kovar pins. The Fe$^{3+}$ satellites are present in both spectra but the Fe$^{2+}$ satellites are not.](image-url)
5.3.4 Raman spectroscopy

As discussed in Chapter 2, Raman spectroscopy can be used to differentiate between different (Co, Fe, Ni)$_3$O$_4$ spinel structures.

Raman spectra from Kovar pins oxidised at 700 °C and 800 °C are shown in Figure 5.6. The spectra contain the characteristic peaks at about 470 cm$^{-1}$ and 695 cm$^{-1}$ that are present in the CoFe$_2$O$_4$ spectrum. The other peaks in the observed spectra are consistent with the Fe$_2$O$_3$ Raman spectrum. Thus, spectra from the oxidised Kovar appear to be combinations of these two spectra.

The spectra for the oxide formed at 700 °C and 800 °C show many similarities but are not identical. The spectrum from the 800 °C oxide is missing some of the peaks associated with Fe$_2$O$_3$ that are present in the 700 °C spectrum, namely the peaks at 224 cm$^{-1}$ and 411 cm$^{-1}$ are not observed, and the peak at 295 cm$^{-1}$ is diminished. In the 600-700 cm$^{-1}$ region there are a number of peaks, a shoulder at 624 cm$^{-1}$ is expected on the 695 cm$^{-1}$ CoFe$_2$O$_4$ peak but also an Fe$_2$O$_3$ peak at 614 cm$^{-1}$, the peak at about 611 cm$^{-1}$ in the 700 °C spectrum is diminished in the 800 °C spectrum, but interpretation is challenging. The peak at 500 cm$^{-1}$ does not appear in the spectrum of the oxide formed at 700 °C but appears as a small shoulder in the 800 °C spectrum. The reduced contribution of the Fe$_2$O$_3$ signal is believed to be a result of decreased Fe$_2$O$_3$ content in the volume of oxide sampled by Raman spectroscopy.

In addition to the peaks from CoFe$_2$O$_4$ and Fe$_2$O$_3$ there are possibly some weak peaks from Fe$_3$O$_4$ which appear in the recorded spectra as shoulders on main peaks. A peak at about 550 cm$^{-1}$ is visible and a peak at 670 cm$^{-1}$, although this peak is hard to differentiate from a peak at around the same position in the Fe$_2$O$_3$ spectrum, and it only appears as a shoulder to the much stronger CoFe$_2$O$_4$ peak at 695 cm$^{-1}$.
5.3. The Kovar oxide layer

The Raman spectroscopy confirms that the oxide layer contains (Co, Fe, Ni)$_3$O$_4$ with at least some cobalt or nickel. However, it cannot distinguish the exact composition of the spinels and cannot quantify the relative amounts of one spinel or another. Raman spectroscopy is expected to have a analysis depth of the order of a few micrometres so variations at different depths within the oxide layer cannot be studied. It also indicates that there is Fe$_2$O$_3$ in the oxide layer, and does not exclude the possibility of some Fe$_3$O$_4$.

![Raman spectra from Kovar pins oxidised at 700 °C and 800 °C, and spectra from Fe$_2$O$_3$ [91] and CoFe$_2$O$_4$ [13].](image)

Raman spectroscopy is known to damage and alter the sample in some cases, and it has been shown that Fe$_3$O$_4$ can be converted to α-Fe$_2$O$_3$ [18] [95]. Shebanova
and Lazor reported that the alterations in their sample only began at laser powers of 20 mW and above. In the work presented here spectra were collected with the lowest energy possible in the instrument available (the lowest beam energy used was approximately 2 mW, a 0.2 mW beam was not powerful enough to give a signal with usable peaks. The spot size was approximately 1 µm. The power was then increased incrementally up to the maximum and the spectra were monitored to check for peaks disappearing/becoming weaker, or new peaks appearing, which would indicate that the oxide had been altered. No changes in the spectra were observed, (although this does not rule out that the sample was damaged with even the lowest energy). In addition, no visible changes to the sample were observed, even with the highest laser energies (an alteration from Fe$_3$O$_4$ to Fe$_2$O$_3$ may result in a change in the oxide colour from grey to red brown).

5.3.5 Microscopy of the surface

The plate samples oxidised at both 700 °C and 800 °C showed an increased degree of oxidation along the grain boundaries resulting in a ridge of oxide along these features, as can be seen in Figure 5.7.

The oxidised wires exhibited a different surface morphology to the plates, as shown in Figure 5.8. This is probably a result of the different surface finish and heat treatment during manufacture as well as the stresses induced in the oxide growing on the wires. As the metal diffuses outward the radius of the underlying metal is decreased and thus stresses are induced within the oxide. The stress can be relieved by spalling, creation of cavities within or under the oxide or buckling of the oxide, which was seen in many areas of the oxides on the pins. It is also possible that there may be slight variations in the composition of the different samples, which may alter the oxide formation.
5.3. The Kovar oxide layer

Figure 5.7: Secondary electron micrographs of Kovar plates oxidised in air for 10 minutes at 700 °C (left) or 10 minutes at 800 °C (right).

Figure 5.8: Secondary electron micrographs of Kovar pins oxidised in air for 10 minutes at 700 °C (left) or 10 minutes at 800 °C (right).

Whiskers were observed on the wires, both those heated at 700 °C and 800 °C. An example is shown in Figure 5.9. Whiskers can grow when there are crystal dislocations in the oxide layer, and since the wires are in the as drawn state and have a damaged and work hardened outer layer the surface contains many dislocations.
Figure 5.9: Whisker growth on the oxide grown on a Kovar wire oxidised at 700 °C for 10 minutes in air.

### 5.3.6 Microscopy of cross-sections

**Imaging**

The thicknesses of the oxides on the wires were measured as approximately (2.1 ± 0.6) µm and (4.0 ± 0.2) µm thick, for the oxides grown at 700 °C and 800 °C, respectively. The oxide thickness on the plates was about (1.4 ± 0.2) µm and (3.2 ± 0.4) µm, and this is similar to the pins, within the uncertainties. This oxide thickness is at the lower end, or below, that generally recommended for glass-to-metal sealing with Kovar [77] [1] [66] [16] [54], yet the oxides formed at 800 °C already showed signs of poor adherence. The oxide on the 800 °C wire was easily knocked off if not treated with care, whilst the 700 °C oxide could not be removed with a stainless steel scalpel blade, indicting superior adherence.
Cross-sections of the plates, etched by polishing with colloidal silica, such as that shown in Figure 5.10, confirm that the thickened areas of oxide indeed correspond to intersections of grain boundaries with the surface. There is a porous region beneath the oxide layer which is found on all Kovar samples oxidised at 700 °C or 800 °C, in agreement with observations reported in the literature. The porous layer is visible in Figures 5.10, 5.11, 5.12 and 5.13. In the oxide layers formed at 800 °C it is also possible to see some additional features; since the 800 °C oxide is nearly twice as thick as the 700 °C oxide it is easier to distinguish features within it. There appears to be a layer along the top of the oxide that has slightly different contrast to the rest of the oxide in backscattered electron micrographs, and also has some porosity or cracking delineating it from the rest of the oxide layer. In some areas of the 800 °C oxide layer there is some cracking, such as can be seen in the micrograph in Figure 5.13. This is probably because of the stresses built up in the oxide during the growth (as the oxide has lower metal ion density than the Kovar substrate it has an increased volume).

**Energy dispersive X-ray spectroscopy (EDX) and Wavelength dispersive X-ray spectroscopy (WDX)**

EDX has the advantage that maps can be collected in parallel, ensuring that the same area was analysed in each map and reducing acquisition time. As there is high degree of peak overlap with iron and cobalt primary x-ray transitions (Fe Kα is at 6.40 eV and Fe Kβ is at 7.06 eV, while Co Kα is at 6.93 eV) it was important to collect WDX maps to verify any conclusions drawn from EDX. Thus EDX and WDX maps are complementary. The elemental maps of oxide cross-sections, shown in Figures 5.12 and 5.13, show a number of features which are discussed below.
Figure 5.10: A representative backscattered electron micrograph of a cross-section of Kovar plate oxidised at 700 °C for ten minutes. A thicker oxide is visible on top of the grain boundaries and corresponding porosity is visible below. The grain structure is revealed by polishing with colloidal silica which lightly etches the surface.

Figure 5.11: SEM micrograph of cross section of a Kovar pin oxidised at 700 °C in air for ten minutes.
5.3. *The Kovar oxide layer*

All samples show an iron depleted region beneath the oxide layer, which is correspondingly enriched in nickel and to a lesser extent in cobalt. The iron depleted region is porous and extends along grain boundaries, consistent with the literature. Porosity in this layer is a result of the Kirkendal effect, where vacancies have diffused inwards in the opposite direction to iron diffusing into the growing oxide layer, resulting in the pores developing when vacancies coalesce.

**Phase mapping using principal component analysis**

There is significant overlap of the iron, nickel and cobalt peaks in the EDX spectra of Kovar and the oxide layers which reduces confidence in the EDX data. To mitigate this, phase analysis was performed using Thermo Scientific’s COMPASS software. COMPASS performs principal component analysis on the full data sets, consisting of full spectra at each pixel, rather than simply looking at the the number of counts in a predetermined region of interest assigned to an element. This ensures that there is not a user bias in selecting elements and produces a probability map of identified components. COMPASS can spatially separate components with severe peak overlap and produce spectra for each component which can be quantified and compared with the other areas of the map. The results from COMPASS agree with the EDX and WDX maps in Figures 5.12 and 5.13, showing a cobalt rich top layer, an iron rich layer and one or two layers below with varying nickel and cobalt compositions.

COMPASS maps are shown for the 700 °C and 800 °C oxide layer in Figures 5.14 and Figures 5.15 respectively. They show that there is an enrichment of cobalt at the surface of the oxide layers formed at both 700 °C and 800 °C; the phase contains over 10 at. % cobalt and little or no nickel. Below this is a layer which contains almost exclusively iron and oxygen, with 1 at. % or less nickel and cobalt.
Chapter 5. Kovar oxide and the Kovar to glass-ceramic interface

Figure 5.12: EDX and WDX maps of a cross-section of Kovar wire oxidised at 700 °C for 10 minutes in air. There is an iron depleted / nickel and cobalt enriched layer beneath the oxide layer. Within the oxide layer there are layers with varying iron, cobalt and nickel concentrations; the top layer appears to have elevated cobalt concentration, the layer below is more iron rich and the lowest layer has an intermediate composition.
5.3. The Kovar oxide layer

Figure 5.13: EDX and WDX maps of a cross-section of Kovar wire oxidised at 800 °C for 10 minutes in air. There is an iron depleted / nickel and cobalt enriched layer beneath the oxide layer. The structure is the same as described in Figure 5.12.
The layers labelled as phase three (yellow) and phase four (light blue) in the COMPASS maps in Figures 5.14 and Figures 5.15 have similar composition. However, the nickel concentration decreases with distance from the bulk metal and is often shown as zero in the upper phase (phase four / light blue). The layer could perhaps be thought of as one layer with a varying nickel concentration or as two layers, one with nickel and one without, and when COMPASS is performed on several sites some are given as two layers and others as one. However, the presence of a line of porosity between the two layers in many areas of the oxide indicates that there is a difference between the two layers, with differing compositions and diffusion rates leading to the growth of the porosity.

<table>
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<th>O</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
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<tr>
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<td>-</td>
<td>54</td>
<td>17</td>
<td>30</td>
</tr>
<tr>
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<td>-</td>
<td>32</td>
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<td>Phase 3 (lower bulk oxide layer), yellow</td>
<td>41</td>
<td>47</td>
<td>8</td>
<td>4</td>
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<tr>
<td>Phase 4 (upper bulk oxide layer), light blue</td>
<td>39</td>
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<td>8</td>
<td>-</td>
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<td>Phase 5 (iron rich oxide layer), brown</td>
<td>34</td>
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<td>-</td>
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<tr>
<td>Phase 6 (top layer), blue</td>
<td>22</td>
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<td>9</td>
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<td>Phase 7, red</td>
<td>11</td>
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Figure 5.14: Left, SEM micrograph of a cross section through the oxide formed on Kovar when oxidised at 700 °C for 10 minutes. Right, EDX map of the same site analysed using COMPASS to give quantifiable phase maps. The grey area at the top is the mounting material. Values in at. %, where a value is given as - the element was not detected.
All of the oxides have a metal (Fe, Co, Ni) to oxygen ratio (0.7-0.9) according to the COMPASS maps and other EDX point analyses indicating that they are most likely to be (Co,Fe,Ni)$_3$O$_4$ rather than (Fe$_2$O$_3$, FeO or CoO).

However, it is expected that the oxygen will be under accounted for in the quantification because the samples were gold coated. The samples had to be gold coated for analysis because, even with carbon coating, there were signs of charging, leading to drift, which was unacceptable as it was necessary to acquire maps for more than a few minutes. As oxygen is a lighter element than the iron, nickel and cobalt its K-α line (used for the quantification) is lower energy and so the corresponding x-rays will be attenuated by the gold layer more easily than the

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<th>Phases</th>
<th>O</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase 1 (bulk), pink</td>
<td></td>
<td>52</td>
<td>17</td>
<td>27</td>
<td>1</td>
</tr>
<tr>
<td>Phase 2 (iron depleted layer), green</td>
<td>4</td>
<td>29</td>
<td>19</td>
<td>47</td>
<td>1</td>
</tr>
<tr>
<td>Phase 3 (lower bulk oxide layer), yellow</td>
<td>45</td>
<td>48</td>
<td>-</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>Phase 4 (upper bulk oxide layer), light blue</td>
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<td>42</td>
<td>12</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Phase 5 (iron rich oxide layer), brown</td>
<td>32</td>
<td>66</td>
<td>-</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Phase 6 (top layer), blue</td>
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<td>74</td>
<td>17</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>Phase 7, red</td>
<td>16</td>
<td>315</td>
<td>13</td>
<td>34</td>
<td>1</td>
</tr>
</tbody>
</table>

Figure 5.15: Left, SEM micrograph of a cross section through the oxide formed on Kovar when oxidised at 800 °C for 10 minutes. Right, EDX map of the same site analysed using COMPASS to give quantifiable phase maps. The grey area at the top is the mounting material. Values in at. %, where a value is given as - the element was not detected.
higher energy x-rays from the metals. This could not be corrected for in the software used and will lead to an under quantification of oxygen in the EDX and COMPASS data. Using the L lines of the metals for quantification may reduce this issue to some degree but increases problems with peak overlap, which would require intensive WDX analysis with suitable standards which was not possible during this project.

5.3.7 Scanning Transmission Electron Microscopy

Since the layers in the oxides are thinner than a micrometre it was decided to use STEM to confirm the results of the COMPASS maps. A foil was made, by FIB milling, from a pin oxidised at 700 °C for 10 minutes. A bright field STEM micrograph is shown in Figure 5.16 and EDX maps are shown (along with a micrograph) in Figure 5.17.

STEM confirms that there is a thin layer of 200 - 300 nm at the top surface of the oxide that is enriched in cobalt. An EDX line scan is shown in Figure 5.18. EDX data are given in Figure 5.19, showing that the top layer has a cobalt concentration of around 12 at. %, higher than the approximately 8 at. % cobalt found for this layer by COMPASS EDX maps, but of similar magnitude. These data also confirm the existence of the layer below, which contains no cobalt or nickel, only iron and oxygen, and is about 300 - 400 nm wide. The EDX also confirms the presence of the two other layers, one containing iron, cobalt and oxygen, the other containing nickel as well.
Figure 5.16: Bright field STEM micrograph of the oxide formed on Kovar oxidised in air for 10 minutes. The top dark layer is the protective platinum layer needed for FIB milling to make the foil. The oxide layer appears to have four layers and beneath the oxide layer the usual porous region is visible.
Figure 5.17: Bright field STEM micrograph and EDX maps (of cobalt, iron, oxygen and nickel) of the oxide formed on Kovar oxidised at 700 °C in air for 10 minutes.
5.3. The Kovar oxide layer

Figure 5.18: a) A bright field STEM micrograph showing the site for an EDX line scan, b) EDX line scan across the oxide layer and into the bulk
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<table>
<thead>
<tr>
<th>Region</th>
<th>O</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>V</th>
<th>Cu</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site 1, top layer</td>
<td>49.6</td>
<td>32.9</td>
<td>14.9</td>
<td>-</td>
<td>0.5</td>
<td>5.6</td>
<td>3.3</td>
</tr>
<tr>
<td>Site 2, second layer</td>
<td>47.8</td>
<td>46.5</td>
<td>-</td>
<td>-</td>
<td>0.2</td>
<td>3.5</td>
<td>2.0</td>
</tr>
<tr>
<td>Site 3, upper bulk</td>
<td>43.1</td>
<td>42.7</td>
<td>8.2</td>
<td>-</td>
<td>0.1</td>
<td>3.6</td>
<td>2.1</td>
</tr>
<tr>
<td>Site 4, lower bulk</td>
<td>41.4</td>
<td>40.9</td>
<td>8.2</td>
<td>3.5</td>
<td>0.1</td>
<td>3.7</td>
<td>2.2</td>
</tr>
<tr>
<td>Below the oxide</td>
<td>-</td>
<td>24.6</td>
<td>19.9</td>
<td>45.1</td>
<td>0.1</td>
<td>6.4</td>
<td>3.9</td>
</tr>
</tbody>
</table>

Figure 5.19: Bright field STEM micrograph of the Kovar oxide, oxidised at 700 °C in air for 10 minutes. Where - is given, the element was not detected.
5.3.8 Microscopy of the fractured oxide layer

The results reported in this chapter appeared to agree with the assumption, based on the current understanding of Kovar oxidation in the literature, that the oxide grows in a continuous process. However, since it has been observed that the oxide is not always well adhered to the bulk and it has been hypothesised that it sometimes buckles during oxidation, it is suggested that a second oxide layer may grow in the void between the underlying metal and the initial oxide layer. In order to understand this process, a pin oxidised at 700 °C for ten minutes was immersed in liquid nitrogen for ten minutes, to promote brittle fracture in the oxide, and then struck with a hammer to fracture the oxide. Some areas of the oxide remained adhered while others spalled off. Scanning electron microscopy of this sample revealed that there were areas where a second oxide layer had formed underneath the first oxide, presumably when it had buckled and become detached.

This work also confirms that the porosity between the layers within the oxide in polished cross-sections and FIB cross-sections is not a result of polishing effects or pull-out. The top, cobalt rich, layer can be clearly seen in Figure 5.20, as can the porosity between the two bottom layers. Figure 5.21 shows an area of the oxide that has buckled and a new oxide has begun to grow on the underside, in the void below. Figures 5.22 and 5.23 show areas where a second oxide has grown on top of the bulk metal after the oxide has buckled away, but remained attached elsewhere and created a void below. The process for the growth of the oxide in the voids beneath (or within) the oxide has the potential to be markedly different since the partial pressure of oxygen will be much lower. This may lead to the formation of a different oxide that is not normally found in the Kovar oxide layer.
Chapter 5. Kovar oxide and the Kovar to glass-ceramic interface

Figure 5.20: Secondary electron micrograph of the fractured Kovar oxide layer. The layered structure is clearly seen, as is a line of porosity between two of the layers.

Figure 5.21: Secondary electron micrograph of the fractured Kovar oxide layer. Oxide crystals have grown on the underside of the oxide after it buckled away from the underlying metal.
5.3. The Kovar oxide layer

Figure 5.22: Secondary electron micrograph of the fractured Kovar oxide layer, where the oxide has buckled up and another oxide layer has grown in the void below.

Figure 5.23: Secondary electron micrograph of the fractured Kovar oxide layer. Three regions are visible: at the top of the micrograph is the oxide that forms initially on the bulk Kovar, at the bottom of the micrograph is the porous region that forms below the oxide layer, across the middle the oxide layer that has formed between the initial oxide layer and the bulk after the initial oxide buckled away from the underlying metal.
5.3.9 Thermodynamics and phase diagrams

The iron - cobalt - oxygen system has been studied by many authors and phase diagrams are available for this system. Two recent (and broadly similar) calculated phase diagrams for iron and cobalt in air are shown in Figures 5.24 and 5.25. The Co/(Co+Fe) ratio in Kovar is approximately 0.24 (since it contains 54 wt. % iron and 17 wt. % cobalt). At the temperatures used for oxidation in this work (700 °C and 800 °C) both phase diagrams indicate that a mixture of spinel and corundum structured $\text{Fe}_2\text{O}_3$ are expected. Although this interpretation should be treated with caution since, the phase diagrams are for equilibrium conditions and the oxide layer will not be in equilibrium while it is growing, it is in agreement with all of the experimental evidence that points to the presence of $\text{Fe}_2\text{O}_3$ and $(\text{Co}, \text{Fe})_3\text{O}_4$ in the oxide. The spinel phase in these works can vary from pure $\text{Fe}_3\text{O}_4$ to pure $\text{Co}_3\text{O}_4$. Zhang and Chen [123] report that the $\text{CoFe}_2\text{O}_4$ spinel is stable down to room temperature, in agreement with experimental results [85, 19, 72], but in disagreement with Jung et al. [41].

When the oxide buckles away from the surface and leaves behind voids, in which a new oxide grows, the partial pressure of oxygen will be much lower than in air in this region. If the log$P_{\text{O}_2}$ falls below about -7 then $\text{Fe}_2\text{O}_3$ will not be thermodynamically favourable and if it falls below about -14 then it will begin to become thermodynamically favourable to form halite / cobaltowustite / $(\text{Co}, \text{Fe})_{1-\delta}\text{O}$, as can be seen in Figure 5.26.
5.3. The Kovar oxide layer

Figure 5.24: Calculated phase diagram of Fe-Co-O system, in air, Jung et al [41]. The region of interest in this study is indicated with a star.

Figure 5.25: Calculated phase diagram of Co-Fe-O, after Zhang and Chen [123]. The region of interest in this study is indicated with a star.
5.3.10 Discussion

The oxide layer that forms on Kovar when it is heated in air for ten minutes at either 700 °C or 800 °C appears to be composed of the same phases; the oxide layer grown at 800 °C was thicker than the oxide layer grown at 700 °C, (4.0 ± 0.2) µm and (2.1 ± 0.6) µm thick, respectively. The oxide has a layered structure which appears to consist of (Co, Fe, Ni)$_3$O$_4$ with varying Fe:Co:Ni ratios and Fe$_2$O$_3$. A schematic diagram of the oxide structure is shown in Figure 5.27.

The top layer (layer 1 in Figure 5.27) can be analysed by all of the techniques available in this study (XPS, Raman, XRD, SEM, STEM) and the combined finding is that this layer is (Fe, Co)$_3$O$_4$. XPS rules out the presence of Fe$_3$O$_4$.
in this layer as only the Fe$^{3+}$ satellite was detected, and not the Fe$^{2+}$. EDX from STEM shows this layer to have at. % Fe 33, Co 15, O 39, (although the COMPASS SEM EDX maps are useful, the quantification is likely to be less accurate than the STEM quantification since this layer is only $\sim$200 nm thick). This Fe:Co ratio (of 11:5) is close to the 2:1 ratio that would be found in CoFe$_2$O$_4$. The presence of the CoFe$_2$O$_4$ phase is further supported by the Raman

Figure 5.27: Schematic diagram of the structure of the oxide and underlying layers in the Kovar. Approximate thicknesses based on oxidation for 10 minutes at 700 °C.
spectroscopy and is also in agreement with the XRD pattern (which was indexed initially as Fe$_3$O$_4$ but could also have been indexed as CoFe$_2$O$_4$.

The second layer (layer 2 in Figure 5.27) cannot be analysed by XPS, but can be by the other techniques (Raman, XRD, SEM, STEM). It is shown by SEM and STEM to be composed of an iron oxide, perhaps with a very small cobalt content (less than 1at. %). EDX in STEM shows this layer to contain no cobalt or nickel but it may be present in low concentrations that were not detected. STEM EDX shows 47 at. % Fe and 48 at. % O. Initially this may appear to indicate that this layer is FeO. However, FeO was not detected by Raman spectroscopy or XRD (both of which would be expected to have an analysis depth that would include this layer since the top layer is only $\sim$200 nm thick). The EDX analysis of every layer in the oxide reveals less oxygen than would be expected; most analyses show more metal than oxygen. Thus even though EDX gives a 1:1 ratio it does not mean that this layer is FeO. In fact, this is the lowest Fe:O ratio of all of the layers, so it is not unreasonable to expect that it is Fe$_2$O$_3$ since it is the iron oxide with the lowest Fe:O ratio. If this layer is indeed Fe$_2$O$_3$ then this explains the results obtained by Raman spectroscopy, and XRD, which both show Fe$_2$O$_3$ to be present. Since cobalt has no solubility in Fe$_2$O$_3$ [123] it is not surprising that this layer contains no cobalt.

The third layer (layer 3 in Figure 5.27) can be analysed by SEM and STEM (including EDX and WDX). EDX, WDX and COMPASS maps all show that it contains both iron and cobalt, and oxygen, but no nickel. It is thought to be a (Fe,Co)$_3$O$_4$ spinel with varying cobalt content.

This fourth (layer 4 in Figure 5.27) can also be analysed by SEM and STEM (including EDX and WDS). EDX, WDS and COMPASS maps all show that the composition appears very similar to the layer above it, but with the addition of
5.4. Argon treated oxide layer

around 3 at. % nickel. It is thought to be a \((\text{Fe, Co, Ni})_3\text{O}_4\) spinel with varying cobalt and nickel content.

There is a region below the oxide (layer 5 in Figure 5.27) that is depleted in iron and enriched in nickel and to a lesser extent cobalt. This is in agreement with the literature, and is an expected result of the high iron content of the oxide layer (since the iron has diffused away from this region and in to the oxide layer). The composition of this layer is approximately 45-50 at. % Ni, 25-30 at. % Fe and 20-25 at. % Co.

Below the iron depleted region is bulk Kovar, shown as layer 6 in Figure 5.27.

This proposed structure is consistent with all of the experimental data, and was observed on multiple samples, but is in disagreement with the previous literature.

5.4 Argon treated oxide layer

5.4.1 SEM, EDX, WDS and COMPASS mapping

During sealing, the pre-oxidised pins are heated again, in an argon atmosphere. There is the possibility that this second heat treatment may change the oxide layer. As such it was decided to oxidise some Kovar pins as usual (at both 700 °C and 800 °C) and then put them through a simulated sealing run (i.e. to heat them under argon to 800 °C). Representative micrographs of cross-sections of these pins are shown in Figure 5.28, followed by a COMPASS map, Figure 5.29, and EDX/WDS maps in Figure 5.30.

The use of COMPASS indicated that the inclusions contain cobalt, iron and oxygen, however they are typically less than 200 nm across, so they are much smaller than the interaction volume of the 15 keV electron beam, such that the
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Figure 5.28: Micrographs of the argon treated oxide layer, initial oxidation of 10 minutes at 700 °C (left) or 800 °C (right). Both samples show the same changes in the oxide layer, i.e. the growth of the light grey inclusions and the disappearance of the layered structure. Note that the scale is different for the two images since the oxide is different thicknesses as a result of the different oxidation temperatures.

Figure 5.29: An SEM micrograph, left, and COMPASS phase map, right, of a section of the Kovar oxide layer (oxidised at 800 °C and then heated in argon). Quantification of the phases is given in the table, in at. %. - indicates that the element was not detected.

<table>
<thead>
<tr>
<th>Phase</th>
<th>O</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase 1 (bulk), pink</td>
<td>-</td>
<td>52.6</td>
<td>16.3</td>
<td>28.6</td>
<td>1.5</td>
</tr>
<tr>
<td>Phase 2 (iron depleted layer), green</td>
<td>3.9</td>
<td>33.7</td>
<td>19.7</td>
<td>40.1</td>
<td>1.5</td>
</tr>
<tr>
<td>Phase 3 (bulk oxide layer), yellow</td>
<td>53.2</td>
<td>43.6</td>
<td>-</td>
<td>1.5</td>
<td>0.9</td>
</tr>
<tr>
<td>Phase 4 (inclusions), blue</td>
<td>37.4</td>
<td>38.0</td>
<td>22.8</td>
<td>-</td>
<td>1.2</td>
</tr>
<tr>
<td>Phase 5, red</td>
<td>17.4</td>
<td>40.8</td>
<td>12.8</td>
<td>26.1</td>
<td>1.3</td>
</tr>
</tbody>
</table>
5.4. Argon treated oxide layer

Figure 5.30: EDX and WDX maps of the oxide on a Kovar pin oxidised at 800 °C for 10 minutes in air and later put through simulated sealing run involving heating to 800 °C in argon.
signal will include some of the x-rays from the rest of the oxide. Considering the unprocessed EDX and WDS maps in Figure 5.30 it is clear that the inclusions are rich in cobalt and poor in iron and oxygen, perhaps containing no iron or oxygen. The inclusions nearer to the bulk metal appear to have some nickel in them, and they must have formed with more nickel around them since the original oxide layer had more nickel closer to the bulk.

It is interesting to note that the oxide phase formed by argon treatment is 53 at. % O, 44 % Fe, which, although it is a higher iron to oxygen ratio than Fe$_3$O$_4$ or Fe$_2$O$_3$ (it is 0.83, compared with 0.75 for Fe$_3$O$_4$ and 0.66 for Fe$_2$O$_3$) it is much closer to an expected ratio than in the initial oxides (which contained more metal then oxygen). The quantification is still thought to be inaccurate as a result of having gold coated the samples, so cannot be relied upon to determine the composition of the oxide.

5.4.2 XPS

XPS was performed on a pin that had been oxidised at 700 °C and then undergone the argon treatment. The survey spectrum from a Kovar pin oxidised to 700 °C for 10 minutes is shown in Figure 5.31. Spectra of the Fe2p region, an example of which is shown in Figure 5.32, were the same as those observed in the as-oxidised pins, with the Fe$^{3+}$ satellite present but the Fe$^{2+}$ satellite not present. Only small amounts of cobalt were detected, and no nickel was detected.

Given that the top layer of the oxide is exposed to air, after having formed in argon, it is possible that it may react with oxygen and alter its oxidation state, especially since Fe$_2$O$_3$ has a higher oxygen ratio than Fe$_3$O$_4$. It has been shown that the top few layers of Fe$_3$O$_4$ are richer in Fe$^{3+}$ than the bulk and this alters the appearance of the iron Fe2p spectrum [12] [44]. An example of such variation
5.4. Argon treated oxide layer

Figure 5.31: XPS survey spectrum of a Kovar pin oxidised at 700 °C and then argon treated.

Figure 5.32: XPS spectrum of the Fe2p region, for a pin oxidised at 700 °C for 10 minutes and then put through a simulated sealing run (heating to 800 °C in an argon atmosphere). The shape of the spectrum indicates that, as with the oxides before argon treatment, the Fe$^{3+}$ satellite is present and Fe$^{2+}$ satellite is not. The position where the absent Fe$^{2+}$ satellite would be is indicated by the arrow.
is shown in Figure 5.33 which shows the Fe2p spectra from Fe$_3$O$_4$ before and after surface oxidation with oxygen plasma. This may explain why the Fe$^{2+}$ satellite is not seen in XPS despite all of the other analysis techniques pointing to the oxide being Fe$_3$O$_4$.

Etching the oxide layer, using Ar$^+$ ions, was attempted to look for variations of oxidation state, but this proved problematic. The oxide did not etch evenly and there was the possibility of the preferential etching of one element and also that the ion bombardment may alter the oxidation state of the metals. Following only 30 seconds of etching the oxidation state of the iron had changed from Fe$^{3+}$ to Fe$^{2+}$. This was, however, considered to be reduction of the oxide by etching rather than a result of etching through to a layer with a different oxidation state.

![Figure 5.33: XPS spectra of Fe$_3$O$_4$ showing that, following surface oxidation, that the Fe$^{3+}$ satellite is seen rather then the Fe$^{2+}$ despite the bulk composition of the sample [12].](image)
5.4.3 Raman spectroscopy

Raman spectroscopy was also performed on the argon-treated pins. The spectra from pins oxidised at both 700 °C and 800 °C, and then put through the argon treatment, are shown in Figure 5.34 overlaid with example spectra from CoFe$_2$O$_4$, Fe$_3$O$_4$ and Fe$_2$O$_3$. The spectrum of the 700 °C pin appears to have peaks only from Fe$_3$O$_4$, while the spectrum from the 800 °C pin has the peaks from Fe$_3$O$_4$ with an additional peak at around 470 cm$^{-1}$ that aligns with the second most intense peak from the CoFe$_2$O$_4$ spectrum (the most intense CoFe$_2$O$_4$ peak is aligned with the intense peak from Fe$_3$O$_4$ so they are expected to be combined if both are present). This indicates that the oxide is predominantly formed of Fe$_3$O$_4$, at least to the depth that is sampled by Raman spectroscopy. The Raman spectrum from FeO does not contain the bands at about 300 cm$^{-1}$ and 535 cm$^{-1}$, and thus FeO does not appear to be present.

Figure 5.34: Raman spectra of Kovar pins oxidised for ten minutes at either 700 °C or 800 °C and then heated in argon, with spectra from CoFe$_2$O$_4$, Fe$_2$O$_3$, and Fe$_3$O$_4$ for comparison. The spectra from the argon treated oxides no longer show the characteristics of CoFe$_2$O$_4$ and Fe$_2$O$_3$ but instead show the characteristics of Fe$_3$O$_4$ with perhaps some CoFe$_2$O$_4$ in the case of the 800 °C.
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5.4.4 Discussion

The oxide appears to change in structure and composition when it is subjected to the argon treatment. It changes from a multi-phase layered structure to a simple oxide phase with inclusions of metallic cobalt and nickel. The oxide appears to be Fe$_3$O$_4$, since it is shown by EDX to contain iron and oxygen and Raman spectroscopy shows that Fe$_3$O$_4$ is present, but Fe$_2$O$_3$ and (Fe,Co)$_3$O$_4$ are not. XPS data are also in agreement with this, since the top layer of Fe$_3$O$_4$ has been shown to have a different Fe$^{2+}$ and Fe$^{3+}$ content to the bulk. If it is assumed that the COMPASS phase map quantification is reasonably reliable then the iron:oxygen ratio (of 0.82) is closer to Fe$_3$O$_4$ then either FeO or Fe$_2$O$_3$. Jung et al., (2004) state that it is common for CoFe$_2$O$_4$ to transform to Fe$_2$O$_3$ or cobaltowustite (Co,Fe)$_{1−δ}$O during annealing at 500 - 800 °C. Figure 5.26 illustrates that lowering the partial pressure of oxygen can stop the formation of Fe$_2$O$_3$. This may explain why, when the oxide is annealed in argon, the Fe$_2$O$_3$ decomposes to Fe$_3$O$_4$.

As can be seen in the Ellingham diagram shown in Figure 5.35, the free energy of formation of Fe$_3$O$_4$ (and FeO) is more negative than that of either NiO or CoO so it is reasonable to propose that during the argon heat treatment the iron in the oxide may reduce the cobalt and nickel that were present in the oxide. The reduced, metallic cobalt and nickel then form the inclusions that are seen in the argon treated oxide layer.

The potential effect of the sealing stage, usually performed in an inert atmosphere such as argon, is not normally considered when discussing the oxide layer on a metal that is to be sealed to glass. However, there is some work by Zanchetta et al. [122], which considered the effect of heating in argon. They reported that some “grey spots appear in the alloy, coming from the porous perturbed interfacial zone” and the oxide layer becomes less complex. When heating to 800 °C
they reported, based on XRD data, that the hematite disappears and a wüstite like phase containing some cobalt appears, with the Fe$_3$O$_4$ phase remaining with an increased lattice parameter. Although the work from Zanchetta is not fully in agreement with the results in this work, it is interesting to note that others have observed the growth of “grey spots” after heating the Kovar oxide layer in an argon atmosphere. The effect of heating in an inert atmosphere during sealing should be considered more thoroughly when developing sealing recommendations as reheating the oxide can have a significant effect on its composition and structure which has the potential for large effects on the resulting seals.

Figure 5.35: Ellingham diagram, showing the free energies of formation of, amongst others, FeO, Fe$_2$O$_3$, Fe$_3$O$_4$, CoO and NiO [51].
5.5 Characterisation of seals made with pre-oxidised Kovar

5.5.1 Production and hermeticity

The seals used in this project\(^2\) were checked for hermeticity, as described in Chapter 3, and in the case of seals made with Kovar pins pre-oxidised at 700 °C for ten minutes or 800 °C for 10 minutes they were found to be hermetic. This is in contrast to those made without pre-oxidising the Kovar.

Seals could be produced more reliably with the pins pre-oxidised at 700 °C, which was thought to be a result of the better adherence of the oxide formed at 700 °C as compared with 800 °C. Therefore, seals for the wider study were made using the 700 °C oxidation treatment, and as such they were the ones that were characterised in this project.

5.5.2 Scanning electron microscopy

Initial characterisation of the hermetic seals, made with pre-oxidised Kovar pins, was by SEM of polished cross-sections. These showed that the oxide had partially dissolved into the glass-ceramic in places, and fully dissolved in others. There was a band of glass-ceramic around the pin that contained iron. This band showed reduced crystallisation, sometimes being completely glassy. Micrographs showing the various conditions at the interface are shown in Figures 5.36 - 5.40. Where the oxide is not fully dissolved it is frequently not in contact with the pin, but is instead separated by a layer of glass that has penetrated beneath the oxide, as seen in Figure 5.40. The cracking that ran around the pin to glass-ceramic interface

\(^2\)seals made by Martyn Staff
5.5. Characterisation of seals made with pre-oxidised Kovar

Figure 5.36: Polished cross-section of a seal. Kovar pin left and glass-ceramic right.

in the seals made without pre-oxidising the pins was not observed, showing that the bonding had been improved.

The distance of iron diffusion into the glass-ceramic varies but is typically around 20-40 µm, as can be seen in Figure 5.41 which shows an iron EDX map overlaid onto an SEM micrograph. It is clear from this map that the distance that the iron diffuses into the glass is not uniform along the interface and that the iron is not found in areas where the glass-ceramic has crystallised. Figure 5.42 shows a series of points that were used for EDX analysis to show the diffusion distance of iron in the glass-ceramic and also the concentration at different distances from the Kovar pin. Iron concentration is typically around 8 to 10 at. % within 10 µm of the interface and drops to zero within 50 µm of the interface.

Where the oxide has not fully dissolved, the metallic inclusions that were observed in the argon treated oxide in Section 5.4 were observed in the oxide. This shows
that the oxide can be altered before it is able to dissolve. With the experimental set up available it was not possible to stop the sealing process part way though, for example by quenching with cold argon, so it is not possible to know for sure whether the oxide begins to dissolve into the glass-ceramic before or after its structure begins to alter from being re-heated. Since the bonding across the interface will be able to change whilst the glass / glass-ceramic is above $T_g$ the altered nature of the oxide is important. Little or no cobalt is detected in the glass near to the oxides, which may indicate that the oxide is able to rearrange before the cobalt containing top layer begins to dissolve.
5.5. Characterisation of seals made with pre-oxidised Kovar

Figure 5.38: In some areas crystals extend up to or from the interface. Iron is not found in the crystals, but is found in the glassy areas surrounding the crystals (in the region close to the pin).

Figure 5.39: An example of an area where the Kovar oxide has fully dissolved, no residual oxide remains on the surface of the pin.
Figure 5.40: An example of a seal where the oxide has separated from the underlying Kovar pin. Glass can be seen between the oxide layer and the pin. Some crystals have formed in this region.

Figure 5.41: An EDX map for iron (red), overlaid on to a micrograph of the pin to glass-ceramic interface. The pin is the solid red area on the right of the micrograph.
5.5. Characterisation of seals made with pre-oxidised Kovar

<table>
<thead>
<tr>
<th>Point</th>
<th>1</th>
<th>2</th>
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<th>7</th>
<th>8</th>
<th>9</th>
<th>10-15</th>
</tr>
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<td>Iron, at. %</td>
<td>8.6</td>
<td>8.6</td>
<td>1.7</td>
<td>5.5</td>
<td>3.4</td>
<td>0.5</td>
<td>0.0</td>
<td>0.7</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Figure 5.42: SEM micrograph with the regions from which EDX point spectra were acquired highlighted, iron concentrations given below.

5.5.3 Pin pull testing and microscopy

Pin pull tests were performed on seals made with pre-oxidised Kovar so that they could be compared with the tests performed on the seals made with non-oxidised Kovar. Whereas the pins without pre-oxidation had almost no signs of adhered glass, the pins that had been oxidised had large areas where the glass was attached, as can be seen in Figures 5.43, 5.44 and 5.45. This indicates that the bonding across this interface was improved significantly.
Chapter 5. Kovar oxide and the Kovar to glass-ceramic interface

Figure 5.43: Kovar pin (pre-oxidised at 700 °C for 10 minutes before sealing) that has been pulled from the glass-ceramic during a pin pull test. The bottom half of the pin in the micrograph was not in contact with the glass, the top half was in contact with glass in the seal and glass can be seen adhered to the pin in this area. There is noticeable charging on the glass as it is thick and non conductive.

Figure 5.44: A higher magnification micrograph of the pin shown in Figure 5.43. Regions of glass are seen adhering to the pin, but there are also regions where the failure has occurred below the oxide layer and metal is visible.
5.5. Characterisation of seals made with pre-oxidised Kovar

Figure 5.45: By imaging from the side it is possible to see a cross-section through the fractured layers. The top is glass with the undissolved oxide layer below it and then the porous iron depleted Kovar beneath that.

5.5.4 STEM

A foil was made from a cross-section of an intact seal, using FIB milling, that spanned the Kovar to glass-ceramic interface. Micrographs of the foil (Figures 5.46 - 5.49) show the same features that were seen with SEM: the porous iron depleted layer, beneath the oxide on the Kovar, the partially dissolved oxide layer and glass containing iron that has dissolved from the oxide layer. Within the oxide layer, the metallic precipitates that were observed in the SEM analysis of foils and the argon treated pins are seen again.

EDX data from an area of glass approximately 1 µm from the oxide layer show this glass to contain (in at. %) 36 % oxygen, 38 % strontium, 12 % aluminium, and 12 % iron. Background signals from copper and titanium were not included in quantification. Boron is not included as it cannot be detected using EDX.
Figure 5.46: Secondary electron STEM micrograph of a foil which spans the Kovar to glass-ceramic interface. On the left is the bulk Kovar (1), then there is the iron depleted nickel rich layer (2) formed beneath the oxide layer, then glass (3) which has penetrated beneath the oxide layer. Near the right is the undissolved oxide layer (4), followed by more glass on the right of the foil (5). Along the top, and penetrating down a crack between the glass and iron depleted region, is the platinum strap used during FIB milling.

Figure 5.47: Z contrast STEM micrograph of the foil shown in Figure 5.46
5.5. Characterisation of seals made with pre-oxidised Kovar

Figure 5.48: Transmission mode STEM micrograph of the Kovar interface foil.

Figure 5.49: Z contrast STEM micrograph centred on the undissolved Kovar oxide layer. The inclusions are clearly visible, as is some grain like structure.
5.6 Conclusions

Having determined that the SRBAL glass-ceramic would bond to Ti-6Al-4V it was important to ensure that it could also be made to bond to Kovar (since Kovar is an essential component in the seals because few other metals have the appropriate thermal expansion). Initially the glass-ceramic did not bond to Kovar, but following pre-oxidation treatment it was possible to make successful hermetic seals.

The oxide on Kovar was characterised so that the interfacial reactions could be better understood. Contrary to the established literature, the oxide formed on Kovar was found to display a high degree of complexity. Through a combination of X-ray photoelectron spectroscopy, X-ray diffraction, Raman spectroscopy, scanning electron microscopy and scanning transmission electron microscopy it was shown that the oxide layer that grows on the Kovar wire samples, when oxidised in air for 10 minutes at either 700 °C or 800 °C, is a multi layered oxide. The first (top) layer is a (Fe, Co)$_3$O$_4$ spinel, the second layer is Fe$_2$O$_3$, the third a (Fe, Co)$_3$O$_4$ spinel with lower Co content and the fourth a (Fe, Co, Ni)$_3$O$_4$ spinel. Beneath the oxide layer a porous, iron-depleted, and nickel and cobalt enriched, layer is formed. In areas where the oxide buckles away from the pin, but remains intact, a second oxide layer can form in the void between the oxide and the bulk.

Bonding between the pre-oxidised Kovar and SRBAL glass-ceramic was confirmed by a number of tests. Hermetic seals could be made, with a helium leak rate of $10^{-9}$ mbar l s$^{-1}$ or less, polished cross-sections of the seals did not have cracking around the pin (or in other areas of the glass-ceramic) and there was glass adhered to the pins after they were pulled from the seals in pin pull tests.

The multi layered oxide structure, and secondary oxide formation in some areas, may explain why, when seals are cross-sectioned and examined with SEM,
5.6. Conclusions

there are areas where the oxide fully dissolves and areas where it is only partially dissolved. In both regions, iron is found in the glass-ceramic near to the pin (for distances ranging from about 10 µm to about 40 µm) and this region shows reduced crystallisation. The dissolution of the oxide is in line with the recommendations in literature for creating glass-to-metal seals. Iron in the glass-ceramic adjacent to the pin can promote bonding in the manner discussed by Pask [78], namely that metal ions in the glass are able to bond metallically to the metal in the pin. In addition, the iron in the glass is believed to increase the thermal expansion of the glass-ceramic in this region. Some preliminary work showed that adding 5 wt. % of iron to the normal SRBAL glass-ceramic increased the thermal expansion from $6.5 \times 10^{-6} \, ^\circ\text{C}^{-1}$ to $10.7 \times 10^{-6} \, ^\circ\text{C}^{-1}$. This is consistent with the finding that, as reported in Chapter 3, the glassy SRBAL has a higher CTE ($9.8 \times 10^{-6} \, ^\circ\text{C}^{-1}$) than the glass-ceramic form. The increased CTE will improve bonding by grading the CTE change across the interface and also, since the CTE is higher than the glass-ceramic, it will increase the radial compression around the interface.

The oxide is clearly altered during the sealing stage (heating to 800 °C in argon). When the oxide is treated in isolation from the glass-ceramic it is altered from the four-layered structure described above to an Fe$_3$O$_4$ layer with inclusions of unoxidised cobalt and nickel. The impact of this in the dissolution of the oxide into the glass-ceramic and the bonding between the pin/undissolved oxide and the iron containing glass-ceramic is not clear.

It is not obvious whether the oxide layer begins to alter before or after the glass is able to flow over, and beneath, it. However, whilst the temperature is above $T_g$ bonding across the interface can still change and iron can diffuse into the glass-ceramic. It is also possible that the oxide begins to dissolve and then later alters structure. However, there is little or no cobalt found dissolved in the glass near
the pin in seals which may indicate that the cobalt rich top layer has begun to rearrange before it has dissolved in to the glass. If the rearrangement of the metal ions within the oxide occurs rapidly enough then the oxide may be an Fe₃O₄ layer with little to no cobalt contained in the spinel structure, with the cobalt instead having migrated into the metallic inclusions. In some areas the oxide appears to have fully dissolved but there are still metallic cobalt or nickel particles, like those found in the argon treated oxide layer, in the glass-ceramic indicating that the oxide had been able to rearrange before dissolving fully.
Chapter 6

Discussion: Characterising glass-to-metal interfaces

The model of bonding first proposed by Pask [78] and illustrated in Figure 2.2 was only intended to provide an overview and a starting point for the discussion, and further study, of glass-to-metal sealing, but it is often used as the main way to discuss the nature of bonding across glass-to-metal interfaces. The model proposes three potential types of interfaces; the first being where there is a thick metal oxide, which is bonded on one side to the metal and on the other side to the glass (which contains dissolved metal ions), the second, and most favourable, where there is a very thin oxide that is bonded to the metal and the metal ion containing glass and the third where there is no oxide layer on the metal and no metal dissolved into the glass (and bonding does not occur). Since it is a simplified ideal model it misses many of the complexities that are needed to understand the interfaces in a real seal. For example, in the work presented in this study the two interfaces are very different to each other. In the case of the titanium to glass-ceramic interface, despite the fact that it appears initially to be a very sharp
Chapter 6. Discussion: Characterising glass-to-metal interfaces

interface that may fall into the most favourable category of interfaces in the Pask model (having only an extremely thin oxide layer on the metal that bonds to the glass) the interface does not fit well in to any of the categories. There is an interaction layer at the interface that creates a titanium boride layer that must be bonded to both the titanium on one side and the glass-ceramic on the other, since it is hermetic. It is the integrity and bonding of this layer that determines the quality of the seal. When considering the bonding at this interface it is necessary to consider the metal-metal bonding of titanium to titanium boride rather than titanium to titanium oxide. It appears, based on the experimental work, that the bonding of this titanium boride layer to the titanium alloy is stronger than the bonding of the titanium boride to the glass, since failure always occurs either in the glass or at the boride-glass interface. The condition of saturating the glass with titanium cannot, and need not, be fulfilled, since the formation of the boride layer prevents diffusion of metal in to the glass.

The glass-ceramic to Kovar interface is also difficult to fit in to any of the models provided by Pask, usually used to discuss the interfaces in glass-to-metal seals. Whilst the oxide layer formed during pre-oxidation does dissolve to some degree the dissolution is not consistent. In some areas it dissolves fully and the model is applicable. There is a region of glass near to the metal which contains close to 10 at. % iron and it is possible that the bonding can occur through the mechanism of metal ions in the glass bonding to the metal in the pin. The oxide may, however, have fully dissolved and the bond may be closer to the situation described in the third case, where the bonding is occurring without an intermediate oxide layer. Along much of the interface the oxide has not fully dissolved. This case may appear to fit in to the first case in the model, but there are inconsistencies. The oxide-to-metal junction is often penetrated by glass during the sealing process, resulting in an interfacial zone that contains: metal, glass (con-
taining dissolved iron), metal oxide, glass / glass-ceramic containing iron. This means that there are several interfaces that need to be considered (metal:glass, glass:oxide, oxide:glass). There are also crystals in the glass that extend up to the interface. This presents another set of interfaces that need to be considered, and since iron is not present in the crystals, the possible bonding at these interfaces cannot be via dissolved metal ions in the glass-ceramic.

In addition, the oxide is altered by the sealing process so that a simple consideration of the oxide formed prior to sealing is not sufficient to fully know (if the oxide has not dissolved into the glass-ceramic) what the oxide is that is bonding to the glass. It is sometimes mentioned the some oxides are more favourable for glass-to-metal sealing than others. For example, FeO is a network modifier and thus not desirable on a metal intended for a glass-to-metal seal, but since the sealing conditions can, and will, alter the oxide, it is not be enough to specify only the oxidation conditions but it is important also to specify sealing conditions since these may alter the oxide to give an undesirable form, or alter an unfavourable oxide into a favourable one. Since altering the sealing conditions will also tend to alter the final properties of the glass-ceramic this may not always be a simple step.

Given the number of possible interfaces that need to be considered, it is hard to construct a simplified model that can describe the system. It is clear that the bonding at the interface is not the only factor determining whether or not a seal will be hermetic; the stress-state at the interface and within the rest of the seal is extremely important. Without favourable stress distributions in the seal it is unlikely to be successful even when there is bonding across the glass-to-metal interface. However, it is clear that pre-oxidation of metal components does improve bonding, as has been shown by decades of study and practical experience, and with Kovar, pre-oxidation is probably essential to produce an hermetic seal.
The thermodynamic and chemical approaches to bonding, while certainly useful, are not sufficient in themselves and the microstructural features of the interface must be considered as well. The dendritic structure of the titanium boride is an important factor in determining seal strength. The impact of the thermal expansion of the components is normally mentioned but the consideration often extends only to the bulk properties of the materials and often, though not always, the interfacial changes are not considered in detail. Given that it is known that oxide layers on metal components dissolve into the glass during sealing and the glass in this region will have an altered coefficient of thermal expansion more consideration should be given to deliberately tailoring this region to improve sealing. Altering the oxide thickness, and perhaps its content and oxidation state, can be used to change the properties of the glass in the interface region and the distance over which the properties of the glass are altered. More use could be made of modelling in order to optimise the stresses, particularly in more complicated seal geometries such as multi-pin components.
Chapter 7

Conclusions

The broad aim of the project at the outset was to characterise the two principle interfaces in a Ti-6Al-4V - boroaluminate glass-ceramic - Kovar seal. The objectives, as given in Chapter 1, were to:

1. characterise the reactions that occur between titanium and the boroaluminate glass-ceramic during sealing
2. identify the oxide that forms on Kovar pins when oxidised in air
3. characterise the reactions that occur between Kovar and the boroaluminate glass-ceramic during sealing
4. draw conclusions regarding the nature of the bonding, to assist in forming satisfactory glass-to-metal seals in this system as well as other systems

These have been met, and the main conclusions are presented below. Those working on the parallel project produced seals with a variety of processing conditions which were characterised and parameters determined that would lead to a
hermetic seal between Ti-6Al-4V, a strontium aluminoborate glass-ceramic and Kovar (a ferrous alloy). The conditions decided upon were: pre-oxidising the Kovar at 700 °C in air for ten minutes prior to sealing, heating the seals by 20 °C per minute from room temperature up to 600 °C then at 10 °C per minute to 800 °C and holding for 20 minutes, then cooling to 500 °C at 5 °C per minute and then back to room temperature at 2 °C per minute.

The presence of a titanium boride layer at the interface of Ti-6Al-4V and a strontium aluminoborate glass-ceramic has been identified. The layer was observed using scanning transmission electron microscopy and shown to be approximately 50 nm thick. Electron energy loss spectroscopy (EELS) showed that the layer contained primarily boron and titanium, with little oxygen. EELS also showed that titanium had not to diffused distances of greater than approximately 50 nm into the glass, and boron had not diffused into the Ti-6Al-4V. The energy of the boron peak measured by wavelength dispersive x-ray spectroscopy, performed on the boride layer exposed by fracturing sections from the seals, was shifted from \( \sim 182 \text{ eV} \) in the glass-ceramic to \( \sim 184 \text{ eV} \) when the boride layer was examined. This peak energy was the same as for boron in a sample of TiB\(_2\), giving further evidence for the existence of this boride layer. This type of interface does not fit in to the model proposed by Pask [78] but there is still bonding across this interface and the seals were hermetic.

Although the study of the interfaces was the primary aim at the beginning of the project, it became a major concern during the work that the oxide on Kovar (that is needed for bonding) did not conform with the available literature. Through the application of many complementary techniques the established view of the oxidation has been challenged. It was shown that pre-oxidation of the Kovar gave a hermetic seal (compared with a non hermetic seal without pre-oxidation) and the oxide layer was studied. It was shown to contain four layers, an observation
that has not been reported in the literature before. The oxide was shown to contain a top layer of (Fe,Co)$_3$O$_4$, with a layer of Fe$_2$O$_3$ beneath it and two layers of (Fe,Co,Ni)$_3$O$_4$ spinel beneath that. The (Fe,Co,Ni)$_3$O$_4$ spinel is not usually reported in the oxide layer on Kovar (most literature reports an iron oxide). The characterisation of the oxide layer was much more thorough than is usual on oxides to be used for glass-to-metal sealing and this process would be useful for other work in this area.

The oxide on Kovar was shown to be altered during the sealing process, or argon annealing, changing from the layered (Fe,Co)$_3$O$_4$, Fe$_2$O$_3$, (Fe,Co,Ni)$_3$O$_4$ layered structure to Fe$_3$O$_4$ (with inclusions of metallic cobalt and nickel).

The strength and hermeticity of the Kovar to glass-ceramic interface is due to a combination of chemical bonding, between the iron containing glass and the underlying Kovar, and the improvement of the stress state around the interface due to the increased coefficient of thermal expansion of the glass-ceramic that contains iron compared with the non iron containing glass-ceramic.
Chapter 8

Future Work

There are three main areas of this study that could be taken forward; the study of the oxide layer grown on Kovar, the study of the interfaces and reactions between the glass / glass-ceramic and the metals and the production of better seals.

The work on the Kovar oxide layer shows that the oxide is not always as simple as is presumed. It would be useful to use the series of techniques that were used in this work to characterise the oxide grown on Kovar under a greater range of conditions, over a range of temperatures and times and with a variety of different samples, for example flat plates, wires of different dimensions, and on samples that have undergone different processing and heat treatments prior to their oxidation. Whilst the work in this study does not agree with much of the literature it would be interesting to reproduce some of the range of work in the literature and characterise the oxide using more extensive methods to determine the nature of the oxides produced in these conditions. The differences observed may have been down to sample geometry, variations in sample composition or other factors and a comprehensive study could certainly add to this area.

Fully characterising the bonding across the Kovar-glass-ceramic interface down
to an atomic scale using more thin foil microscopy and electron energy loss spectroscopy, whilst possibly desirable, is problematic since preparing samples that are thin enough to give sharp well defined spectra without also damaging the material and altering the bonding state of the elements is difficult at best. As such, this kind of analysis was not performed in this work and inferences about the nature of the bonding must be drawn from a combination of theory and other experimental data. Future work using these techniques may be able to give insight into the exact nature of the bonding between the metal / oxide and the glass / glass-ceramic.

It would potentially be useful to produce seals that were made using the start of the sealing process but quenched to room temperature with argon to stop the reactions part way through, for example heating the seals up to 800 °C, holding for 20 minutes and then quenching rapidly down to room temperature so that the effect of the prolonged cooling stage can be separated and the order of different reactions separated, for instance dissolution of the Kovar oxide and crystallisation of the glass-ceramic. This would require a different furnace set up to the one used in this work.

When considering the seals as a whole and aiming to produce better seals, a greater theoretical consideration would be a good place to focus future efforts. Finite element analysis could be used to show which set of processing parameters would give the glass-ceramic the optimum coefficient of thermal expansion to give the best stress distribution in the seals. The stresses in the seal are of upmost importance and, therefore, improvements in this area have the potential to have a large positive impact in seal manufacture. It should, however, be noted that any modeling needs to consider the varying properties of the materials, particularly the glass-ceramic. For example, the region of glass-ceramic containing dissolved iron has a different coefficient of thermal expansion to the bulk and different
proportion of crystals, and also has a varying iron content and therefore a varying coefficient of thermal expansion. The oxide on Kovar, and the iron depleated region beneath it, would also need to be considered.

Although there are several ways in which the work could be extended, the larger study, of which this work was a part, has been successful in producing hermetic glass-to-metal seals with titanium housings.
References


[23] I. Donald, P. Mallinson, B. Metcalfe, L. Gerrard, and J. Fernie. Recent developments in the preparation, characterization and applications of glass-


[51] R. V. Kumar. DoITPoMS, University of Cambridge [Online], Available www.doitpoms.ac.uk/tlplib/ellingham_diagrams/ellingham.php. 131


[116] L. Wei. Wetting & interface studies of boroaluminate glasses on Ti, Nilo48, Nilo52, Kovar alloys. AWE Joining Symposium, Surrey University, 2013. 13, 36


References