Evolution of the interfacial phases in $\text{Al}_2\text{O}_3$–Kovar® joints brazed using a Ag–Cu–Ti-based alloy

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Abstract

A systematic investigation of the brazing of $\text{Al}_2\text{O}_3$ to Kovar® (Fe–29Ni–17Co wt.% ) using the active braze alloy (ABA) Ag–35.25Cu–1.75Ti wt.% has been undertaken to study the chemical reactions at the interfaces of the joints. The extent to which silica-based secondary phases in the $\text{Al}_2\text{O}_3$ participate in the reactions at the ABA/$\text{Al}_2\text{O}_3$ interface has been clarified. Another aspect of this work has been to determine the influence of various brazing parameters, such as the peak temperature, $T_p$, and time at $T_p$, $\tau$, on the resultant microstructure. As a consequence, the microstructural evolution of the joints as a function of $T_p$ and $\tau$ is discussed in some detail.

The formation of a $\text{Fe}_2\text{Ti}$ layer on the Kovar® and its growth, along with adjacent $\text{Ni}_3\text{Ti}$ particles in the ABA, dominate the microstructural developments at the ABA/Kovar® interface. The presence of Kovar® next to the ABA does not change the intrinsic chemical reactions occurring at the ABA/$\text{Al}_2\text{O}_3$ interface. However, the extent of these reactions is limited if the purity of the $\text{Al}_2\text{O}_3$ is high, and so it is necessary to have some silica-rich secondary phase in the $\text{Al}_2\text{O}_3$ to facilitate the formation of a $\text{Ti}_3\text{Cu}_3\text{O}$ layer on the $\text{Al}_2\text{O}_3$. Breakdown of the $\text{Ti}_3\text{Cu}_3\text{O}$ layer, together with fracture of the $\text{Fe}_2\text{Ti}$ layer and separation of this layer from the Kovar®, has been avoided by brazing at temperatures close to the liquidus temperature of the ABA for short periods of time, e.g. for $T_p$ between 820 and 830 °C and $\tau$ between 2 and 8 min.

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1. Introduction

Alumina is widely used in the electronics, refractory ceramics and automotive industries [1]. A connection to a metal is often required in a number of applications for this ceramic. An example of such a connection can be found in a spark plug, where a steel casing is shrink-fitted around the alumina [2]. Other feedthrough assemblies, such as those used in sensors to measure pressures in aircraft systems, require chemically bonded metal–alumina interfaces to produce hermetic bonds.

Joining a ceramic to a metal is particularly difficult. This is because ceramics typically have a significantly lower coefficient of thermal expansion (CTE) than metals. A consequence of the CTE mismatch is the development of stresses near a joint, particularly at the free surfaces of the joined components as the joint is cooled from the bonding temperature [3]. In some cases, these stresses can lead to failure of the joint, even with good chemical bonding at the metal/ceramic interface [4]. One method used to help alleviate the effects of a CTE mismatch between the alumina and the metal is to bond the alumina to an intermediate material that has a similar CTE and a lower elastic modulus. An iron-nickel-cobalt alloy with a composition of approximately Fe–29Ni–17Co wt.%, also known commercially as Kovar®, is used in feedthrough devices for the transition between the alumina and metal. The CTE of Kovar® between room temperature and its Curie temperature (T_c) of ~435 °C is ~5.5×10⁻⁶ K⁻¹ [5] (for this range of temperature the CTEs for >85 wt.% α–Al₂O₃-based ceramics vary between ~5.5 and ~9.0×10⁻⁶ K⁻¹ [6]). There is a discontinuous change in the CTE of Kovar® to a noticeably higher value for temperatures above its T_c [5]. The thermally-induced stresses in an alumina–Kovar® joint can sometimes be accommodated by using eutectic Ag–28Cu wt.%-based braze alloys to achieve a bond [7].

Active metal brazing is a relatively simple technique to join alumina to a metal or to itself. In this technique, the braze alloy has a small quantity of an element added so that it can react with the alumina to form compounds at the braze/alumina interface to enable the liquid braze to spread over the ceramic surface. The added element is known as an active element and the braze alloy is called an active braze alloy (ABA). As a consequence, a processing step to modify the bonding surface of the alumina
chemically to make it more wettable by a conventional braze alloy, such as the Ag–Cu eutectic alloy, is avoided. Such a process can involve several complex steps to achieve a suitable ‘metallised’ surface on the alumina; the sintered metal powder process known as the moly–manganese process is an example [8,9].

In the literature, active metal brazing of alumina to Kovar® has typically been reported using Ag–Cu eutectic or near–eutectic alloys with added Ti as the active element, at a level of about 1.5–5 wt.%. The chemical reactions that occur between Al2O3 and two Ag–Cu–Ti-based ABAs with quantities of Ti in this range, known by their trade names of Cusil ABA® (Ag–35.25Cu–1.75Ti wt.%) and Ticusil® (Ag–26.7Cu–4.5Ti wt.%), have recently been investigated in some detail [10]. A typical brazing procedure to join ≥95 wt.% Al2O3 to itself using these two ABAs results in a metastable layered structure at the Ag–Cu–Ti/Al2O3 interface that is primarily comprised of Ti3Cu3O, which is in contact with the ABA, alongside a thin γ-TiO layer on the Al2O3 [11]. By comparison with what is now known about this interface, there is a lack of detailed knowledge about the chemical processes at the ABA/Al2O3 interface in Al2O3–Kovar® joints brazed with Ag–Cu–Ti-based ABAs. This is partly because during brazing the chemical elements in the Kovar® react immediately with the Ti in the ABA. As a consequence, this limits the amount of reaction product(s) formed at the Ag–Cu–Ti/Al2O3 interface. Either a thin reaction layer, typically ≤1 μm in width, or small individual particles are found at this latter interface. Therefore, it is difficult to analyse the interfacial phase(s) for their crystal structure or composition using techniques such as X-ray diffraction (XRD) or energy-dispersive X-ray spectroscopy (EDS) in a scanning electron microscope (SEM).

The work of Stephens et al. [12–14] indicates that it is essential to have a continuous reaction layer at both the Ag–Cu–Ti/Al2O3 interface and the Ag–Cu–Ti/Kovar® interface to form hermetic Al2O3–Kovar® joints. In their work, the phase that forms at this interface is referred to as Ti5O3, although no conclusive experimental evidence was reported to suggest it is indeed a titanium oxide. Schilm et al. [15] have observed a 0.7–1 μm thick continuous layer on 96 wt.% Al2O3 after joining to Kovar® using a 50 μm thick Cusil ABA® foil and a brazing cycle that peaked at 830 °C for 10 min. The precise chemical composition of this layer is not given, but it is reported to
contain Ti and O, along with small quantities of Fe, Ni and Co from the Kovar®. The composition of a reaction layer that formed on the Al₂O₃ in a joint which was held at 850 °C for 10 min has been reported to be 36.6Ti–25.0Ni–12.6Fe–4.7Co–4.3Cu–4.1Al–12.5O–1.3Ag wt.% (note there is an error in this composition because the total percentage by mass exceeds 100%). Wang et al. [16] also have measured significant quantities of elements from the Kovar®, particularly Ni and Fe, in a continuous 1–2 μm thick reaction layer. This layer formed on 95 wt.% Al₂O₃ which was joined to Kovar® using a 100 μm thick Cusil ABA® foil and with a brazing cycle that peaked at 900 °C for 5 min. The formation of a particularly thick layer can be attributed to brazing at a high peak temperature with a thicker ABA. Wang et al. [16] suggest that this reaction layer is TiO based on its chemical composition of 38.8Ti–15.5Ni–8.9Fe–2.8Co–5.5Cu–6.9Al–18.0O–2.2Si at.% and XRD data collected from the Ag–Cu–Ti/Al₂O₃ interface. It is anticipated that the reaction layer itself contains significant quantities of the elements from the Kovar®, particularly Ni and Fe, because the quantities of these elements in the phases such as Al₂O₃, Ag and Cu surrounding the reaction layer are expected to be low. Furthermore, there is no evidence of another phase containing the chemical elements of the Kovar® next to the reaction layer. These observations suggest that either a titanium oxide is forming on the Al₂O₃ that can accommodate considerable quantities of Ni and Fe or a more chemically complex phase is produced.

A reaction layer on the Al₂O₃ was absent in a braze joint that was prepared at a higher temperature of 940 °C by Wang et al. [16]. Instead, large individual Fe₂Ti particles were observed next to the Al₂O₃. This change in the interfacial structure has been explained qualitatively by Wang et al. [16] in terms of the residual amount of Ti in the ABA available to react with the Al₂O₃ after the Ti had first reacted with some of the elements in the Kovar® which had dissolved into the liquid ABA, forming various intermetallic compounds such as Fe₂Ti and Ni₃Ti. The same explanation for the absence of a continuous reaction layer on the Al₂O₃ was first introduced by Stephens et al. [12–14] as a Ti scavenging process, in which the chemical reactions between the ABA and the Kovar® in the initial stages of brazing prevent Ti from diffusing to, and reacting with, the Al₂O₃. The Ti in the ABA should diffuse to both interfaces of the joint after the ABA melts. If the rates of the chemical reactions at the ABA/Kovar®
interface are significantly higher than those occurring at the ABA/Al₂O₃ interface, a significant proportion of the Ti could indeed be consumed to form various intermetallic compounds at the ABA/Kovar® interface before a continuous layer on the ABA forms. The studies by Stephens et al [12] and Wang et al. [16] suggest a continuous reaction layer on the Al₂O₃ forms before breaking down at the peak brazing temperature, and so it might be possible to control the structure of this layer to some extent by carefully selecting the processing conditions. It is apparent that thermal decomposition of the layer on the Al₂O₃ has not been considered. Clearly, further work is required to identify the phase(s) forming on the Al₂O₃. It would also be worthwhile to investigate the stability of the phase(s) at the peak temperature of a brazing cycle to determine the rate of any significant microstructural changes in a joint, particularly at the Ag–Cu–Ti/Al₂O₃ interface.

Two compounds are usually observed in the ABA of Al₂O₃–Kovar® joints, in the form of a complex chain of small micron-sized particles that extends across the joint [13–18]. EDS, and to a much lesser extent XRD, have been used to identify these compounds as Fe₂Ti and Ni₃Ti. Considerable quantities of Fe and Ni, and also other metals such Co or Cu, are typically incorporated in these compounds. This is probably a result of substitution of the Fe or Ni in the two compounds. The work of Schilm et al. [15] suggests that these compounds form on the Kovar® before separating into the ABA. In their work, a Fe–rich layer was observed directly on Kovar® at a Cusil ABA®/Kovar® interface in a 96 wt.% Al₂O₃–Kovar® joint heated to 830 °C for 10 min. This layer was approximately 2–3 μm thick and also contained Ni, Co and Ti. A much thinner Ni–rich layer containing Co, Fe and Ti was also observed between the Fe–rich layer and the ABA. Individual particles containing Ni, Cu and Ti were also identified in the ABA, and they were either in contact with the Ni–rich layer or close to it. However, conclusive experimental evidence identifying all of the phases at the Ag–Cu–Ti/Kovar® interface has not been found. Consequently the chemical processes at this interface are not fully understood.

Very low hermetic yields were obtained by Stephens et al. [12] for joints made with a Kovar® spacer that was brazed between two pieces of 94 wt.% Al₂O₃ using Cusil ABA®. Brazing was performed at temperatures between 810 and 900 °C for 5 to 10
min and also at 850 °C for up to 30 min. Joints that were identified to have hermetically sealed interfaces contained a continuous reaction layer on the \( \text{Al}_2\text{O}_3 \). This continuous reaction layer formed in a small selection of joints that were either brazed for 10 min or less at 850 °C or for 5 min at higher temperatures. The microstructures of these particular joints were not hermetic. All other conditions used produced a discontinuous layer on the \( \text{Al}_2\text{O}_3 \). The joints typically failed at a maximum tensile stress between ~35 and ~80 MPa, which was considered to be satisfactory for the particular application. A correlation between the hermiticity and the tensile strengths of the joints was not identified. The investigations by Stephens et al. [12,13] demonstrate that forming hermetically sealed joints using Cusil ABA\textsuperscript{®} is not straightforward. The difficulties experienced by Stephens et al. [19] in fulfilling this very task ultimately motivated them to develop a new ABA that utilises Zr as the active element specifically to join \( \text{Al}_2\text{O}_3 \) to Kovar\textsuperscript{®}. It is particularly apparent from the work of Stephens et al. [12] and Wang et al. [16] that the interfacial microstructure between the ABA and the \( \text{Al}_2\text{O}_3 \) can be controlled to some extent by altering the peak temperature of the brazing cycle (\( T_p \)) used or time at \( T_p \) (\( \tau \)). It is evident from the available literature that the effects of altering these two variables on the overall microstructure of joints, and the extent to which they result in significant microstructural developments, have not yet been defined clearly.

In the work reported here, a comprehensive evaluation of several \( \text{Al}_2\text{O}_3/\text{Cusil ABA} \)/Kovar\textsuperscript{®} joints using electron microscopy-based techniques has been undertaken to determine conclusively the interfacial reaction products which form over a wide range of conditions. The microstructural characterisation work has been used ultimately to develop a better understanding of the evolution of the interfacial phases. This is particularly important for the phase(s) forming at the Ag–Cu–Ti/\( \text{Al}_2\text{O}_3 \) interface, because it appears that the interfacial phase(s) can break down at high \( T_p \) or by extending \( \tau \) at a specific \( T_p \). 99.7 and 95 wt.% \( \text{Al}_2\text{O}_3 \) have been used to study the extent to which silica-based secondary phases in the \( \text{Al}_2\text{O}_3 \) participate in the chemical reactions at the ABA/\( \text{Al}_2\text{O}_3 \) interface. All of the joints have been prepared using Cusil ABA\textsuperscript{®}, which is a commercially available Ag–Cu–Ti-based ABA containing a relatively low quantity of Ti. It was anticipated that a limited quantity of Ti would
make it less difficult to study the reaction process occurring at the interfaces in the early stages of brazing. This particular Ag–Cu–Ti-based ABA is also widely used for the brazing of Al₂O₃. The effects of altering processing variables such as \( T_p \) and \( \tau \) on the microstructure of the joints prepared with 95 wt.% Al₂O₃ have also been studied.

2. Experimental

2.1. Materials

Cusil ABA® (Ag–35.25Cu–1.75Ti wt.%) has been used to join Kovar® (Fe–29Ni–17Co wt.%) to 95 and 99.7 wt.% Al₂O₃. The ABA was supplied by VBC Group Ltd (UK) in foil form, with a thickness of ~50 μm, from which 10 × 5 mm sections were taken for joining. SEM investigation of the as-received ABA revealed that the active element, Ti, is in the form of Cu₄Ti particles randomly distributed in a Ag–Cu eutectic alloy [10]. The as-received Kovar® was composed of equiaxed grains of various sizes, ranging from ~10 to ~100 μm in width, which have a face-centered cubic crystal structure with a lattice parameter \( a = 3.6 \) Å. No significant changes in the microstructure and the crystal structure of Kovar® were identified after brazing.

Braze joints made with 95 wt.% Al₂O₃ were compared with joints made with high purity 99.7 wt.% Al₂O₃. After polishing and coating with a thin layer of carbon, electron microprobe analysis of the bonding surfaces of these ceramics was performed to determine their composition. A Cameca SX-100 (France) electron microprobe operated at 15 keV with a 10 nA electron beam was used in the wavelength-dispersive mode. Calibration of the elements of interest used several mineral standards. The compositions of the ceramics are given in Table 1. The Si and Ca in the 95 wt.% Al₂O₃ are very likely to be in the form of oxides. EDS and electron diffraction data collected after brazing the 95 wt.% Al₂O₃ to itself shows intergranular amorphous SiO₂ present in the ceramic. Al₂O₃ in the form of 10 × 5 × 4 mm plates were brazed to 10 × 5 × 0.5 mm plates of Kovar®. Prior to brazing, all of the components of a joint were cleaned separately in an ultrasonic bath of detergent for up to 15 min.
2.2. Brazing process

\( \text{Al}_2\text{O}_3 / \text{Cusil ABA}^\text{®} / \text{Kovar}^\text{®} \) joints were prepared in an atmosphere of purified argon, which was established in a horizontal electric furnace (STF 15/450, Carbolite, UK) as described in [10]. The BIP\textsuperscript{®} technology by Air Products and Chemicals (USA) was used to purify the argon gas entering the furnace. A heating rate of 10 °C min\textsuperscript{–1} was used. The cooling rate was \~20 °C min\textsuperscript{–1} between the peak temperature used and \~500 °C, after which it reduced significantly during a furnace cool to room temperature. A pressure of \~4 kPa was applied to all of the joints using a 20 g weight to improve contact across the components.

The combinations of \( T_p \) and \( \tau \) used to braze the two types of \( \text{Al}_2\text{O}_3 \) to Kovar\textsuperscript{®} are given in Table 2. Brazing of 95 wt.% \( \text{Al}_2\text{O}_3 \) was carried out with \( T_p \) ranging from the liquidus temperature of the ABA of 815 °C to 900 °C. For these brazing experiments \( \tau \) varied between 0 and 45 min. The low quantity of secondary phase in 99.7 wt.% \( \text{Al}_2\text{O}_3 \) made it difficult to establish a bond between the \( \text{Al}_2\text{O}_3 \) and the ABA. Consequently, brazing of this ceramic was carried out to a lesser extent, with \( T_p \) ranging from 815 °C to 875 °C and \( \tau \) ranging from 0 to 45 min, as described in Table 2.

2.3. Analytical processes

A field emission SEM, Leo 1530 VP, Leo Electron Microscopy - Carl Zeiss\textsuperscript{®}, Germany, operated at 20 kV was used to observe the microstructures of joints, before undertaking more detailed examinations of joints by transmission electron microscopy. This microscope was equipped with an energy dispersive spectrometer (INCA-7426, Oxford Instruments\textsuperscript{®}, UK), which was particularly useful to analyse the compositions of the phases next to the Kovar\textsuperscript{®}. Typically, four cross-sections of each joint were analysed with this microscope to monitor the homogeneity of the interfacial structures and chemistry across the joint. A low speed diamond saw was used to cut out cross-sections of joints, which were mounted in acrylic resin at room temperature, polished and then coated with a thin layer of carbon before observations were made. It was necessary to mount all of the joints made with 99.7 wt.% \( \text{Al}_2\text{O}_3 \) in clear resin before cutting out cross-sections, because the \( \text{Al}_2\text{O}_3 \) broke away from the ABA while cutting these joints.

A scanning transmission electron microscope (STEM), Tecnai Osiris\textsuperscript{™}, FEI, USA,
operated at 200 kV was also used to perform elemental analysis using an EDS system (Super-X system, FEI, USA). Data from the transmission electron microscopes (TEMs) used in this work were particularly useful to study the very thin interfacial phases developing on the Al$_2$O$_3$. Thin sections of joints were prepared for TEM analysis using a focused ion beam instrument, FIB, (Helios Nanolab™, FEI, USA). The procedure commonly known as the lift-out technique [20] was used to transfer sections of joints up to 25 × 10 μm to molybdenum grids, or a carbon substrate on a molybdenum grid. These sections were subsequently reduced to a thickness of ~100 nm using the FIB.

Selected area diffraction patterns were collected to determine the crystal structures of phases using a conventional TEM (200CX, JEOL®, Japan), which was operated at 200 kV. The camera length of this microscope was monitored at regular intervals using an Al thin film, which was supplied by Agar Scientific, UK.

The thicknesses of the reaction layers were measured as a function of $T_p$ and $\tau$ from images collected using the SEM; a mean value and ± one standard deviation from twenty measurements are reported.

3. Results

3.1. Brazing 95 wt.% Al$_2$O$_3$ to Kovar®

Subtle and progressive changes in the microstructure of joints between 95 wt.% Al$_2$O$_3$ and Kovar® were observed, particularly as a function of $\tau$. Therefore, the microstructural developments at each $T_p$ used are discussed separately as a function of $\tau$.

3.1.1. Brazing 95 wt.% Al$_2$O$_3$ at 815 °C

Back-scattered electron images (BSEIs) of cross-sections of 95 wt.% Al$_2$O$_3$–Kovar® joints that were held at 815 °C for 0 to 45 min are shown in Figures 1 and 2. Heating a joint to 815 °C and then maintaining this temperature for a nominal 1 s before cooling is not sufficient to bond the ABA chemically to the Al$_2$O$_3$. When the ABA melts, the Kovar® immediately reacts with it to form a continuous layer that is about 1.3 μm thick at the ABA/Kovar® interface, as shown in Figure 1a. EDS analysis of this layer
indicated that it is Fe-rich with a typical mean composition of 42Fe–34Ti–11Co–9Ni–4Cu at.%. It was also apparent that there were significant variations in the relative amounts of the elements identified in this layer. The amount of Ti varied between 28 and 35 at.%, which are values that approximately describe the range of compositions for non-stoichiometric Fe₂Ti at ~815 °C according to various Fe–Ti phase diagrams [21,22]. A variation of up to ~10 at.% Fe appeared together with variations in the amounts of Ni, Co or Cu to provide a M:Ti ratio, where M is Fe+Co+Ni+Cu, between 1.9 and 2.6. This variation in composition was not dependent on the distance away from the surface of the Kovar® at which measurements were taken. It is apparent that a significant amount of Fe in this layer is substituted by other transition metals such as Ni, Co and Cu in such a way that a variation in the composition across this layer is complex. As a consequence, it was not possible to obtain experimental evidence for the diffusion of elements across this layer.

This Fe-rich layer on the Kovar® is comprised of crystals which have the same structure as Fe₂Ti (hexagonal, P6₃/mmc, space group 194) with the lattice parameters a = 4.8 Å and c = 7.8 Å. A selection of indexed electron diffraction patterns from these crystals is shown in Figure 3. The diffraction patterns indicate that this layer forms by a chemical reaction between the Kovar® and the ABA to produce a solid solution of Ni, Co and Cu in Fe₂Ti, by substitution of Fe, rather than forming only by the diffusion of elements in the ABA into the Kovar®. The composition of this layer measured by EDS is consistent with the current estimations of the solubility of Co, Ni and Cu in Fe₂Ti at Tp. Between 800 and 900 °C, Fe₂Ti can accommodate ~35 at.% Co and ~20 at.% Ni [23,24]. The solubility of Cu in Fe₂Ti is significantly lower, approximately 3 at.% at 849 °C [25]. Although an accurate descriptor of this layer could be (Fe+Co+Ni+Cu)₂Ti, it is referred to as Fe₂Ti in the text and figures for simplicity.

Small particles, up to 100 nm in diameter, were identified in the Fe₂Ti layer both at grain boundaries and within the Fe₂Ti grains. An annular dark-field image of an ABA/Kovar® interface showing these particles as dark spots in the Fe₂Ti layer, because they have a lower average atomic number than Fe₂Ti, is given in Figure 4, along with the results of EDS area scans containing some of these particles. The EDS measurements indicate that these particles contain Ti. This is consistent with electron
diffraction data which identify the crystal structure of these particles as that of α-Ti (hexagonal, \(P6_3/mmc\), space group 194) with the lattice parameters \(a = 2.9 \, \text{Å}\) and \(c = 4.8 \, \text{Å}\); a selection of indexed electron diffraction patterns is also shown in Figure 4.

There are three different phases in the form of individual particles that appear to nucleate on the Fe\(_2\)Ti layer. One of these phases is typically observed as a number of very small particles forming a thin broken layer directly on the Fe\(_2\)Ti layer (Figure 1a). This phase has a lower average atomic number than Fe\(_2\)Ti, and so it appears darker than the Fe\(_2\)Ti layer in the BSEIs shown in Figure 1a. The composition of this phase was measured by EDS in the STEM, typically as 46Ti–20Fe–16Ni–11Co–6Cu–1Al at.\%.

This phase has a lower average atomic number than Fe\(_2\)Ti, and so it appears darker than the Fe\(_2\)Ti layer in the BSEIs shown in Figure 1a. The composition of this phase was measured by EDS in the STEM, typically as 46Ti–20Fe–16Ni–11Co–6Cu–1Al at.\%. Its crystal structure was identified as that of FeTi (cubic, \(Pm\bar{3}m\), space group 221, \(a = 2.9 \, \text{Å}\)), which is isostructural with CoTi and also a high temperature form of NiTi [26,27]. A selection of indexed electron diffraction patterns from this phase is shown in Figure 5. Extensive substitution of Fe by other similar-sized transition metals such as Ni, Co and Cu also occurs in this phase. This is because FeTi can accommodate a significant amount of Cu at \(T_p\), approximately \(\sim 35\) at.\% at 849 °C [25], and it forms continuous solid solutions with the isostructural compounds CoTi and NiTi between 800 and 900 °C [23,24]. This phase is referred to as FeTi rather than (Fe+Ni+Co+Cu)Ti in the text and figures for simplicity.

The other two phases next to the Fe\(_2\)Ti layer are in the form of particles with a diameter up to \(~350\) nm, being either in contact with the Fe\(_2\)Ti layer or separated from this layer by very small distances. The majority of these particles are Ni-rich, with a typical composition of 48Ni–25Ti–11Cu–9Co–7Fe at.\%. The crystal structure of this phase has been identified as that of Ni\(_3\)Ti (hexagonal, \(P6_3/mmc\), space group 194) with the lattice parameters \(a = 5.2 \, \text{Å}\) and \(c = 8.4 \, \text{Å}\); a selection of indexed electron diffraction patterns from this phase is shown in Figure 6. Although a significant amount of Ni in Ni\(_3\)Ti is substituted by other transition metals such as Cu, Co and Fe, this phase is referred to as Ni\(_3\)Ti for simplicity. A very small proportion of the particles next to the Fe\(_2\)Ti layer in joints which were brazed at 815 °C for a nominal 1 s and indeed at temperatures up to 845 °C for up to 15 min have a composition of 33Cu–31Ni–32Ti–2Co–1Fe–1Al at.\%. These particles were identified as the equiatomic CuNiTi phase (tetragonal, \(I4/mmm\), space group 139) with the lattice parameters \(a = 3.1 \, \text{Å}\) and \(c = 8.0 \, \text{Å}\); a selection of electron indexed diffraction patterns from this phase
is shown in Figure 7.

There are two significant differences in the interfacial structures of the joint after increasing \( \tau \) to 1 min at a \( T_p \) of 815 °C. The first difference is mainly a result of lateral growth of the FeTi particles on the Fe\(_2\)Ti layer to produce a continuous FeTi layer, which is ~330 nm thick. The second difference is the formation of a 650 nm thick, continuous and polycrystalline layer on the Al\(_2\)O\(_3\) to bond the ABA chemically to the Al\(_2\)O\(_3\). These microstructural developments at the ABA/Kovar\textsuperscript{®} and ABA/Al\(_2\)O\(_3\) interfaces can be seen clearly in the BSEIs shown in Figure 1b.

The crystal structure of the particles on the Al\(_2\)O\(_3\) has been identified as that of the diamond-cubic type structure of two M\(_6\)X-type compounds in the Ti–Cu–O system, specifically Ti\(_3\)Cu\(_3\)O and Ti\(_4\)Cu\(_2\)O (cubic, \textit{Fd\textoverline{3}m}, space group 227), having a unit cell length that varies between 11.2 and 11.5 Å. A selection of electron diffraction patterns from these particles is shown in Figure 8. The composition of this phase was found to vary considerably across the layer on the Al\(_2\)O\(_3\). However, no definitive correlation between its composition and the position at which EDS measurements were taken within the layer could be identified. The EDS measurements consistently indicated that the amount of Ti was approximately equal to the amount of other metals in this phase. For example, the compositions of 42Ti–28Cu–6Ni–5Fe–1Co–5Al–12O at.% and 44Ti–15Cu–14Ni–10Fe–3Si–2Al–11O at.% have been measured. These measurements are consistent with the formation of only Ti\(_3\)Cu\(_3\)O on the Al\(_2\)O\(_3\). It is also apparent that some of the Cu in the Ti\(_3\)Cu\(_3\)O has been substituted for other elements, being mainly Fe and Ni. The presence of Si in this layer is very significant, because it indicates that the glassy secondary phase in the alumina has reacted with the ABA. The amount of Si in this layer varied between ~1 and 5 at.%, with the highest value measured at a region close to SiO\(_2\) in the alumina. Based on these experimental results, it is concluded that the layer on the alumina is a solid solution of several elements such as Si, Al, Fe, Ni and Co in Ti\(_3\)Cu\(_3\)O, and so it is referred to as Ti\(_3\)Cu\(_3\)O for simplicity.

A number of isolated particles, some being up to 200 nm in diameter, were found in the Ti\(_3\)Cu\(_3\)O layer at the grain boundaries, and also close to the Al\(_2\)O\(_3\), as shown in Figure 9. The results of an EDS area scan containing one of these particles are also given in Figure 9. The particles contain Ti and O; their chemical composition is
measured as being 67Ti–26O–3Cu–2Fe–1Ni–1Si at.%. Electron diffraction patterns collected from these particles are consistent with a solution of oxygen in α-Ti (hexagonal, \(P6_3/mmc\), space group 194), with the lattice parameters \(a = 2.95\ \text{Å}\) and \(c = 4.85\ \text{Å}\), rather than a Ti–O compound. These particles were not observed in joints that were brazed for 2 min or longer at any \(T_p\) used.

A small number of isolated particles were also observed between the Ti\(_3\)Cu\(_3\)O layer and the Al\(_2\)O\(_3\), as shown in Figure 9. EDS analysis indicated that these particles also contained Ti and O. Electron diffraction was used to identify the crystal structure of these particles as that of γ-TiO (cubic, \(Fm\overline{3}m\), space group 225, \(a = 4.3\ \text{Å}\)); a selection of electron diffraction patterns is shown in Figure 9. γ-TiO particles were observed on the Al\(_2\)O\(_3\) in joints made at a \(T_p\) of 815 °C only as a small number of isolated particles, between \(~30\ \text{nm}\) and \(~150\ \text{nm}\) wide. The Ag–Cu–Ti/Al\(_2\)O\(_3\) interface described here closely resembles the interfacial structures that form in Al\(_2\)O\(_3\)/Ag–Cu–Ti/Al\(_2\)O\(_3\) joints at an early stage of brazing [10].

No further significant changes in the structures of the FeTi, Fe\(_2\)Ti and Ti\(_3\)Cu\(_3\)O layers were identified until \(\tau\) was increased to 10 min at a \(T_p\) of 815 °C. By contrast, some of the Ni\(_3\)Ti particles had grown significantly by brazing for 6 min at 815 °C to form rectangular shaped particles, approximately \(2\ \mu\text{m} \times 1\ \mu\text{m}\) in size. After brazing for 10 min at a \(T_p\) of 815 °C, a thin broken FeTi layer was typically observed alongside the Fe\(_2\)Ti layer, as shown in Figure 1c. A small proportion of the same joint showed no evidence of FeTi on the Fe\(_2\)Ti layer. The thicknesses of the FeTi and Fe\(_2\)Ti layers as a function of \(\tau\) for the different \(T_p\) used are shown graphically in Figure 10. At a \(T_p\) of 815 °C, the thickness of the FeTi layer reduced from \(~350\ \text{nm}\) until it had disappeared as \(\tau\) increased from 6 to 15 min. At the same time, the Fe\(_2\)Ti layer had grown thicker from \(~1.3\) to \(~2.0\ \mu\text{m}\). A correlation between the growth of Fe\(_2\)Ti and the disappearance of FeTi is also found in joints made at a \(T_p\) of 845 °C, in which the FeTi layer was observed alongside the Fe\(_2\)Ti layer only at a brazing time of 2 min. A single continuous layer of Fe\(_2\)Ti was observed on the Kovar\(^\circledR\) consistently in a joint that was held at 815 °C for 15 min, as shown in Figure 1d. Cracks from the Fe\(_2\)Ti/Kovar\(^\circledR\) interface going through the Fe\(_2\)Ti layer to the Fe\(_2\)Ti/ABA interface were occasionally observed in this joint (Figure 1d), and also other joints that were brazed for 15 min or longer at a higher
The microstructure across the joint became irregular after increasing $\tau$ to 30 min at a $T_p$ of 815 °C. Continuous reaction layers of Fe$_2$Ti and Ti$_3$Cu$_3$O were typically seen on the Kovar® and the Al$_2$O$_3$, respectively. However, at random positions along the joint the Fe$_2$Ti layer had separated from the Kovar® carrying Ni$_3$Ti particles with it into the ABA, as shown in Figure 2a. The result is a complex chain of particles, comprised of Fe$_2$Ti and Ni$_3$Ti, in the ABA, which is consistent with reports in the literature [13,14,16–18] of the typical distribution of these phases in a joint. At the same area of the joint, a broken Ti$_3$Cu$_3$O layer is observed on the Al$_2$O$_3$. Separation of the Fe$_2$Ti layer from the Kovar® was also occasionally observed in a joint held for 45 min at a $T_p$ of 815 °C. The Fe$_2$Ti layer typically remained attached to the Kovar® in this joint. At the ABA/Al$_2$O$_3$ interface in the same joint, Fe$_2$Ti particles with the composition 45Fe–31Ti–12Co–11Ni–1Cu at.% were observed between the broken Ti$_3$Cu$_3$O layer and the ABA, as shown in Figure 2b. Those Fe$_2$Ti particles appear to nucleate and grow at the ABA/Al$_2$O$_3$ interface, specifically on the Ti$_3$Cu$_3$O layer as it breaks down, rather than relocate to the ABA/Al$_2$O$_3$ interface from the Fe$_2$Ti layer on the Kovar®. This has been confirmed by brazing at a higher $T_p$ deliberately to decompose the Ti$_3$Cu$_3$O phase completely and produce larger quantities of Fe$_2$Ti particles at the ABA/Al$_2$O$_3$ interface. A detailed account of the decomposition of Ti$_3$Cu$_3$O in braze joints is given later in this section, and the process is discussed in section 4.1.2.

3.1.2. Brazing 95 wt.% Al$_2$O$_3$ at 845 °C

As expected, increasing $T_p$ to 845 °C resulted in less subtle and more progressive changes in the microstructure of the joint as a function of $\tau$. A collection of BSEIs of cross-sections of 95 wt.% Al$_2$O$_3$–Kovar® joints that were held at 845 °C for 2 to 45 min is shown in Figure 11. Continuous reactions layers were observed on both the Kovar® and the Al$_2$O$_3$ only in joints that were brazed at $T_p$ for up to 10 min. Brazing for a short time of 2 min at 845 °C formed interfacial structures that were very similar to those formed in a joint using a $T_p$ of 815 °C. A continuous Fe$_2$Ti layer, ~1.45 μm in thickness, formed on the Kovar®, alongside a 900 nm thick FeTi layer. As $\tau$ increased
to 10 min the FeTi layer disappeared to leave a 2.1 μm thick Fe$_2$Ti layer on the Kovar$^\circledR$. The Ti$_3$Cu$_3$O layer on the Al$_2$O$_3$ became slightly thicker with this change in $\tau$, increasing from ~650 nm to ~750 nm.

Joints that were brazed for 15 min or longer at a $T_p$ of 845 °C contained overly developed ABA/Kovar$^\circledR$ and ABA/Al$_2$O$_3$ interfaces. In these joints, the Fe$_2$Ti layer separated from the Kovar$^\circledR$ taking the Ni$_3$Ti particles with it into the ABA, and/or the Ti$_3$Cu$_3$O layer on the Al$_2$O$_3$ broke down considerably. The Ti$_3$Cu$_3$O phase decomposed completely using a brazing cycle that peaked at 845 °C for 45 min to leave two phases, both being in the form of particles, at the ABA/Al$_2$O$_3$ interface, as shown in Figure 11d. Electron diffraction and TEM–EDS have been used to identify Fe$_2$Ti particles (48Fe–30Ti–10Co–10Ni–2Cu at.%) alongside several nanometre-size $\gamma$-TiO particles (50Ti–48O–1Al–1Si at.%) at this overly developed ABA/Al$_2$O$_3$ interface.

For a $T_p \leq 845$ °C, the Ti$_3$Cu$_3$O layer became thicker as $\tau$ increased to 10 min, up to a maximum value of ~1 μm. Unfortunately, our data does not provide definitive results on the kinetics of reaction layer growth at the ABA/Al$_2$O$_3$ interface. The thickness of this layer reduces as $\tau$ increases further at either $T_p$. This is because the Ti$_3$Cu$_3$O phase is metastable at $T_p$, i.e. between 815 and 900 °C, and so the Ti$_3$Cu$_3$O layer breaks down using long brazing times. The rate of Ti$_3$Cu$_3$O decomposition is accelerated by using a higher $T_p$ and the effect of the decomposition process is very noticeable by brazing for ≥30 min at 815 °C, ≥15 min at 845 °C or ≥2 min at between 875 and 900 °C.

3.1.3. Brazing 95 wt.% Al$_2$O$_3$ at ≥875 °C

A joint with a completely uniform microstructure has not been produced using a $T_p$ ≥875 °C. Brazing for 2 min at either 875 °C or 900 °C resulted in a joint typically having continuous Fe$_2$Ti and Ti$_3$Cu$_3$O layers on the Kovar$^\circledR$ and the Al$_2$O$_3$, respectively. There were also areas of this joint having a broken Ti$_3$Cu$_3$O layer and a Fe$_2$Ti layer separated from the Kovar$^\circledR$. Brazing for 15 min or longer at 875 °C produced ABA/Al$_2$O$_3$ interfaces having either a broken Ti$_3$Cu$_3$O layer with nanometre-size $\gamma$-TiO particles between the Ti$_3$Cu$_3$O and the Al$_2$O$_3$, or Fe$_2$Ti particles on the Al$_2$O$_3$ alongside several smaller $\gamma$-TiO particles when the Ti$_3$Cu$_3$O phase decomposed.
3.2. Brazing 99.7 wt.% $\text{Al}_2\text{O}_3$ to Kovar®

Brazing alumina ceramics containing very low levels of secondary phases to Kovar® was particularly difficult. In all of the joints made using 99.7 wt.% $\text{Al}_2\text{O}_3$, there were some sections where the ABA and $\text{Al}_2\text{O}_3$ were in contact, but where there was no evidence for the formation of any new phases. Furthermore, no evidence was found of a chemical reaction between 99.7 wt.% $\text{Al}_2\text{O}_3$ and the ABA in any joint that was brazed for 2 min at a $T_p \leq 875$ °C or up to 45 min at 815 °C. It would not have been worthwhile to increase $T_p$ to encourage a reaction between the ABA and the $\text{Al}_2\text{O}_3$. This is because the $\text{Fe}_2\text{Ti}$ layer on the Kovar® had already peeled away into the ABA at several positions of a joint that was brazed at 875 °C for 2 min to produce an irregular microstructure. The first sign of a chemical reaction at the ABA/$\text{Al}_2\text{O}_3$ interface was found in a joint which was brazed for 15 min at 845 °C. At a section of this joint, a 450 nm thick $\text{Ti}_3\text{Cu}_3\text{O}$ layer, with the composition $45\text{Ti}–23\text{Cu}–9\text{Ni}–5\text{Fe}–2\text{Co}–2\text{Al}–1\text{Si}–13\text{O}$ at.%., formed on the $\text{Al}_2\text{O}_3$. The $\text{Ti}_3\text{Cu}_3\text{O}$ layer was not continuous across the joint. The microstructure at the ABA/Kovar® interface was also inconsistent across the joint, as a consequence of the $\text{Fe}_2\text{Ti}$ layer being separated from the Kovar® at random positions. A collection of BSEIs capturing some of the interfacial structures produced in 99.7 wt.% $\text{Al}_2\text{O}_3$/Cusil ABA®/Kovar® joints which were brazed at 845 °C for 2 to 45 min is shown in Figure 12. In this composite figure, sections of joints with interfacial phases developed at the ABA/$\text{Al}_2\text{O}_3$ interface are shown intentionally.

Increasing $\tau$ further had an undesirable effect on the structure of the $\text{Ti}_3\text{Cu}_3\text{O}$ layer on the $\text{Al}_2\text{O}_3$. This layer broke down to leave individual $\text{Fe}_2\text{Ti}$ particles between it and the ABA, along with nanometre-size $\gamma$-$\text{TiO}$ particles on the alumina.

These brazing experiments indicate that the glassy secondary phase in the 95 wt.% $\text{Al}_2\text{O}_3$ helps to bond the ceramic chemically to the ABA at the lowest $T_p$ used. Brazing 95 wt.% $\text{Al}_2\text{O}_3$ to Kovar® using Cusil ABA® for short periods of time at temperatures near to the liquidus temperature of the ABA enables a continuous $\text{Ti}_3\text{Cu}_3\text{O}$ layer to form, and be preserved, on the $\text{Al}_2\text{O}_3$, and also produces a uniform interfacial structure.
at the ABA/Kovar® interface.

4. Discussion

4.1. Formation of the interfacial phases

4.1.1. ABA/Kovar® interface

Melting of the ABA facilitates the diffusion of Ti towards the Kovar® and the Al₂O₃. The rates at which chemical reactions occur at the ABA/Kovar® interface are significantly higher than those at the ABA/Al₂O₃ interface. As a consequence, using a very short \( \tau, \ll 1 \) min, only produces chemical bonds between the ABA and Kovar®. A number of binary compounds mainly form on the Kovar® which have one element substituted extensively by several elements from the Kovar® or ABA. Fe₂Ti nucleates first on the Kovar®, presumably by the reaction:

\[
2 \text{Fe} + \text{Ti} \rightarrow \text{Fe}_2\text{Ti} \quad (1)
\]

which has a change in Gibbs free energy (\( \Delta G \)) of approximately \(-71 \) kJ mol\(^{-1}\) at 1100 K (based on the Gibbs free energies reported in the work of Barin [28]). At this temperature, which is only slightly higher than the lowest \( T_p \) used, a reaction producing FeTi is thermodynamically less favourable, based on having a larger \( \Delta G \) (approximately \(-32 \) kJ mol\(^{-1}\)). The Fe₂Ti particles subsequently grow to form a continuous layer on the Kovar®. This layer seems to hinder the diffusion of Ti to the Kovar® significantly, because further growth of this layer normal to the Kovar® appears to cease at a thickness of \(~1.3 \mu\text{m}\).

In this investigation, the extent to which the composition of the compounds identified at the ABA/Kovar® interface are affected by altering \( T_p \) or \( \tau \) is not clear. This is partly because these compounds form as solid solutions containing considerable and highly variable quantities of elements from the ABA and the Kovar®. This apparently occurs by substitution of one of the elements in the compound by an element that is similar in size. A further complication is that some of these compounds, such as Fe₂Ti
and Ni$_3$Ti, can evolve in non-stoichiometric forms [21,27]. The homogeneity of Fe$_2$Ti ranges from ~67 to ~72 at.% Fe at 815 °C, and a number of assessments of the Fe–Ti system suggest this range becomes smaller as temperature decreases [21,22]. In this regard, the particles of α-Ti observed in the Fe$_2$Ti layer could precipitate out of the Fe$_2$Ti on cooling the joints from $T_p$. It is unlikely that these particles are remnants of the active element that has not reacted. This is because similar quantities of α-Ti particles were observed in all of the joints examined by TEM, and also in a 95 wt.% Al$_2$O$_3$–Kovar® joint brazed at 845 °C for 100 min.

Various compounds such as FeTi, Ni$_3$Ti and, to a much lesser extent, CuNiTi subsequently nucleate on the Fe$_2$Ti layer, possibly by the reactions:

\[
\text{Fe + Ti} \rightarrow \text{FeTi} \quad (2)
\]

\[
3 \text{Ni + Ti} \rightarrow \text{Ni}_3\text{Ti} \quad (3)
\]

\[
\text{Cu + Ni + Ti} \rightarrow \text{CuNiTi} \quad (4)
\]

where $\Delta G$ for equation 3 occurring at 1100 K is approximately $-115$ kJ mol$^{-1}$. At this temperature, the formation of other Ni–Ti compounds such as NiTi and Ni$_2$Ti by a reaction between Ni and Ti are less thermodynamically favoured; $\Delta G$ values for the formation of Ni$_2$Ti and NiTi are approximately $-69$ kJ mol$^{-1}$ and $-57$ kJ mol$^{-1}$, respectively. No thermodynamic information could be found on CuNiTi to assess whether reaction 4 is possible at the $T_p$ used. If it is assumed that some extent of local equilibrium exists at the ABA/Kovar® interface so that phase diagrams can be used to explain the development of the interfacial structure, it can be inferred from the Fe–Ni–Ti isothermal section at 800 °C shown in Figure 13 that Fe$_2$Ti can form on the Kovar®. The Kovar® is considered simply as Fe-rich $\gamma$-(Fe,Ni) such as Fe–28 Ni at.%, which is separated from Fe$_2$Ti by the two-phase region $\gamma +$ Fe$_2$Ti. After the formation of Fe$_2$Ti, the formation of FeTi and Ni$_3$Ti simultaneously on the Fe$_2$Ti under equilibrium conditions is possible.

The FeTi particles grow primarily parallel to the Fe$_2$Ti layer to form another
continuous layer. This layer also appears to hinder the diffusion of Ti, now to the Fe$_2$Ti/FeTi interface, because the FeTi layer does not continue to grow significantly after becoming continuous. At this point, chemical reactions begin at the ABA/Al$_2$O$_3$ interface, which are discussed in section 4.1.2. Elements from the Kovar® continue to diffuse towards the ABA, although now being impeded by the Fe$_2$Ti and FeTi layers. The Fe$_2$Ti layer grows significantly thicker, up to ~2 μm, as the FeTi layer disappears. A possible explanation for this is a reaction at the Fe$_2$Ti/FeTi interface between FeTi and the Fe diffusing from the Kovar®, as described in equation 5.

\[
\text{Fe} + \text{FeTi} \rightarrow \text{Fe}_2\text{Ti}
\]  

(5)

This reaction is thermodynamically possible at 1100 K, with a $\Delta G$ of approximately $-39$ kJ mol$^{-1}$. The thicker Fe$_2$Ti layer presents a larger diffusion barrier, and so this layer does not continue to grow after the FeTi has reacted. Diffusion of elements such as Fe, Ni, and Ti through the Fe$_2$Ti layer appears to cease at this point, because the Ni$_3$Ti particles on this layer and the Ti$_3$Cu$_3$O particles on the Al$_2$O$_3$ do not grow further. The evolution of the interfacial phases in an Al$_2$O$_3$/Cusil ABA®/Kovar® joint is summarised by the schematic mechanism in Figure 14.

4.1.2. ABA/Al$_2$O$_3$ interface

The chemical processes that occur between Cusil ABA® and the Al$_2$O$_3$ in Al$_2$O$_3$–Kovar® brazed joints are initially very similar to those occurring in Al$_2$O$_3$–Al$_2$O$_3$ joints made with the same ABA. As a consequence, the microstructures at the ABA/Al$_2$O$_3$ interfaces in both joints are very similar at the early stages of brazing. The chemical processes responsible for joining Al$_2$O$_3$ to itself have recently been reported [10]. Each process is summarised here together with some subtle differences as a consequence of replacing one Al$_2$O$_3$ component by Kovar®.

After the ABA melts, and also sometime after chemical reactions begin at the Kovar® surface, some Ti reacts with the Al$_2$O$_3$ component. This reaction occurs primarily with the secondary phases in the Al$_2$O$_3$ such as SiO$_2$. The resultant products
are Ti₂O, Si (from SiO₂) and, to a much lesser extent, Al (from Al₂O₃). The majority of the Si and Al is dissolved into the molten ABA, and presumably the Ti₂O remains in contact with the Al₂O₃. Particles of Ti₂O were identified as a transient phase in this work, only being observed in a 95 wt.% Al₂O₃–Kovar® joint brazed for 1 min at 815 °C (Figure 9). A thin continuous Ti₂O layer probably develops on the Al₂O₃, which subsequently reacts to form a continuous Ti₃Cu₃O layer on the Al₂O₃. This reaction can be described by the schematic equation:

\[ \text{Ti}_2\text{O} + \text{Ti} + M' \rightarrow \text{Ti}_3\text{M'}_3\text{O} \]  

where M' is a mixture of several elements, comprised mainly of Cu, but also Ni, Fe, Si and Al. In a number of previous studies [15,16], various quantities of elements from the Kovar®, particularly Ni and Fe, were identified in the reaction layer on the Al₂O₃. This is because Ti₃Cu₃O forms on the Al₂O₃, rather than a titanium oxide, and it can accommodate various elements such as Ni and Fe by a substitution mechanism.

Individual γ-TiO particles were observed between the Ti₃Cu₃O layer and the Al₂O₃ rather than a continuous γ-TiO layer. This is a consequence of Ti reacting with the Kovar® first, and so reducing the quantity of Ti in the ABA, which subsequently reacts at the ABA/Al₂O₃ interface. Two recent assessments of the Al₂O₃/Ag–Cu–Ti/Al₂O₃ configuration provided empirical evidence to suggest γ-TiO forms after the Ti₃Cu₃O layer, by a reaction between Al₂O₃ and Ti diffusing through the Ti₃Cu₃O layer [10,11]. Based on this evidence, a similar reaction might also occur with the secondary phase in the Al₂O₃, and so γ-TiO formation could be represented by the schematic equations:

\[ x\text{Ti} + \frac{1}{3}\text{Al}_2\text{O}_3 \rightarrow \text{Ti}_x\text{O} + \frac{2}{3}\text{Al} \]  

\[ x\text{Ti} + \frac{1}{2}\text{SiO}_2 \rightarrow \text{Ti}_x\text{O} + \frac{1}{2}\text{Si} \]

where \( x \approx 1 \), and the Al and Si can form solid solutions with the titanium oxide or Ti₃Cu₃O. Estimations of \( \Delta G \) for equations 7 and 8 occurring at 1100 K are approximately 6 kJ mol⁻¹ and -82 kJ mol⁻¹, respectively, on the basis of oxidation-
reduction reactions alone using crystalline oxides to produce the stoichiometric compound TiO. These estimations suggest the formation of γ-TiO in this work might occur by equation 8 rather than 7. However, such a simple assessment of these equations does not take into account the free energies of solution of Al or Si in the oxides at the ABA/Al₂O₃ interface or the molten ABA. Since the estimation of ΔG for equation 7 is a small positive value, it could therefore be that equation 7 is thermodynamically possible at T_p. No evidence was found of various Si–Ti compounds such as Si₅ Ti, Si₂ Ti and Si₃ Ti₅ at the ABA/Al₂O₃ interface. These Si–Ti compounds are thermodynamically less likely to form at around T_p than TiO; the Gibbs free energies of formation at 1100 K for TiO and these Si–Ti compounds are given in Table 3 on a per mole Ti basis for comparison purposes.

One of the main causes of inhomogeneity in the microstructure of a joint is the breakdown of the Ti₃Cu₃O layer on the Al₂O₃. Ti₃Cu₃O is metastable at T_p and eventually breaks down to produce more γ-TiO particles and new Fe₂Ti particles at the ABA/Al₂O₃ interface. The Fe in these Fe₂Ti particles was originally a solute in Ti₃Cu₃O. Increasing the quantity of Ti in the ABA as an approach to lengthen the time taken before significant decomposition of the Ti₃Cu₃O layer occurs is discussed in section 4.2. In the same section, conditions for T_p and τ to produce Al₂O₃/Cusil ABA®/Kovar® joints with well-developed uniform microstructures are given.

4.2. Morphological features of the interfacial phases and joint strength

It was expected that the thickness of the Ti₃Cu₃O layer would be limited as a consequence of the chemical reactions between the Kovar® and ABA consuming some of the Ti. The maximum thickness of this layer was ~850 nm. This is considerably lower than the maximum thickness of the Ti₃Cu₃O layers formed in a Al₂O₃–Al₂O₃ joint made using the same ABA and ceramic used in this work, which was ~1.5 µm after brazing for 2 min at 875 °C [11]. This difference in thickness is significant because the Ti₃Cu₃O phase is not stable at T_p and as a consequence it breaks down to form other phases at the ABA/Al₂O₃ interface. The temperature at which the chemical decomposition of Ti₃Cu₃O begins should not be affected by its thickness, but a thinner Ti₃Cu₃O layer would break down faster. This could adversely affect the performance
of a joint, particularly if it must be airtight. In the 95 wt.% Al$_2$O$_3$–Kovar$^\circledR$ joint, the Ti$_3$Cu$_3$O layer broke down completely so that there was no evidence of it at the ABA/Al$_2$O$_3$ interface after ~45 min at 845 °C. Only partial decomposition of the Ti$_3$Cu$_3$O layers in a Al$_2$O$_3$–Al$_2$O$_3$ joint made using the same ABA and ceramic occurred after brazing between 845 and 875 °C for the same length of time [11].

It has been shown that continuous Ti$_3$Cu$_3$O layers prevail in Al$_2$O$_3$/Ag–Cu–Ti/Kovar$^\circledR$ joints for longer periods of time at the liquidus temperature of the Ag–Cu–Ti-based ABA by essentially increasing the quantity of the active element [11]. This was achieved by changing the ABA from Cusil ABA$^\circledR$ to Ticusil$^\circledR$. As a consequence, thicker Ti$_3$Cu$_3$O layers formed, and this ultimately lengthened the time taken to break the Ti$_3$Cu$_3$O down into a noticeably broken layer by several minutes. Such a modification to the Al$_2$O$_3$/Ag–Cu–Ti/Kovar$^\circledR$ joint could help to produce a thicker Ti$_3$Cu$_3$O layer, and so preserve it as a continuous layer for longer periods of time at $T_p$. However, this would also have the undesirable effect of increasing the quantity of the brittle phases formed at the ABA/Kovar$^\circledR$ interface.

Another cause of inhomogeneity in the microstructure of a joint is the separation of the Fe$_2$Ti layer from the Kovar$^\circledR$, which typically coincides with the breakdown of the Ti$_3$Cu$_3$O layer on the Al$_2$O$_3$. This occurs after the Fe$_2$Ti layer develops fully into a 2 μm thick layer, together with the development of cracks in this layer. Very little evidence of deformation of Fe$_2$Ti was observed by TEM, suggesting this phase does not help to any significant extent to dissipate any residual stresses in the joint. Breakdown of the Ti$_3$Cu$_3$O layer on the Al$_2$O$_3$, together with fracture and separation of the Fe$_2$Ti layer, can be avoided by brazing joints at temperatures close to the liquidus temperature of the ABA for short periods of time. For this particular joint, this can be achieved using a $T_p$ between 820 and 830 °C and $\tau$ between 2 and 8 min. These conditions should also produce uniform microstructures at both interfaces. In practice, the size of the joint will also influence the precise brazing conditions used. This is because any temperature gradients across the joint should be minimised to achieve a uniform microstructure, and this is harder to achieve as the joint becomes larger.

Braze joints of this type will experience tensile stresses in their application, either by an applied load and/or by any residual stresses. Tensile strengths were measured at
ambient temperature of 95 wt.% Al₂O₃–Kovar®–95 wt.% Al₂O₃ joints, with Cusil ABA® positioned between the Kovar® and Al₂O₃. This particular configuration has been used to follow the ASTM F19 standard method for testing the tensile strength of ceramic–metal and ceramic–ceramic brazed bonds [29]. Therefore, the Al₂O₃ components were in the form of ASTM F19 tensile buttons as described in [29] and [11], and so much larger joints were made compared to those used to study the interfacial reaction processes in these joints. As a consequence, significant temperature gradients developed across some of the larger joints. SEM of the joints showed that the interfacial microstructures were far more developed at the edges of these joints, up to ~300 μm into a joint rather than up to ~10 μm for the smaller-sized joints. Three joints were tested for each brazing condition used. These were a $T_p$ of 814 °C with $\tau$ equal to 2 or 15 min, a $T_p$ of 828 °C with $\tau$ equal to 15 and 45 min, and a $T_p$ of 844 °C with $\tau$ equal to 2, 15 and 45 min. The joints held at 844 °C for 2 min had the highest maximum tensile strengths of the order of 60±15 MPa.

5. Conclusions

The interfaces of several Al₂O₃/Cusil ABA®/Kovar® joints have been assessed using a range of electron microscopy-based techniques to determine the identity of the interfacial phases, the chemical processes leading to their evolution and the influence of various brazing parameters, such as $T_p$ and $\tau$, on their structure.

When the ABA melts, the Kovar® first reacts with it to produce quickly a continuous Fe₂Ti layer on the Kovar®. Various compounds subsequently nucleate on this layer such as FeTi and Ni₃Ti. The FeTi develops into a continuous layer on the Fe₂Ti, with larger Ni₃Ti adjacent to it. This layer eventually breaks down to enable the Fe₂Ti layer to grow further. This development coincides with the formation of cracks across the Fe₂Ti layer. Brazing for long periods of time causes the Fe₂Ti layer to separate from the Kovar® and migrate into the ABA, taking the Ni₃Ti particles with it.

The formation and growth of the interfacial phase at the ABA/Kovar® interface consumes a significant proportion of the Ti in the ABA before reactions at the ABA/Al₂O₃ interface begin. As a consequence, a thinner reaction layer develops on the
Al₂O₃. This layer has been identified as a solid solution of elements from the Kovar® such as Fe and Ni in Ti₃Cu₃O. The formation of Ti₃Cu₃O is facilitated greatly by the glassy secondary phases in the Al₂O₃ such as SiO₂. To a lesser extent, individual γ-TiO nanoparticles were identified on the Al₂O₃. Therefore, the addition of Kovar® next to the ABA does not change the intrinsic chemical reactions occurring at the ABA/Al₂O₃ interface. However, the extent to which the Ti₃Cu₃O layer grows is limited by the presence of the Kovar®. Since Ti₃Cu₃O is metastable at T_p, it consequently breaks down faster, producing more γ-TiO and new Fe₂Ti particles at the ABA/Al₂O₃ interface. Brazing with an ABA containing larger amounts of Ti should produce a thicker Ti₃Cu₃O layer and this might help to prolong its breakdown into a noticeably broken layer.

Brazing of Al₂O₃ to Kovar® with Cusil ABA® has been performed successfully in terms of microstructural development using a ceramic component containing ~5 wt.% secondary phase such as SiO₂. The secondary phase helps to bond the ceramic chemically to the ABA. Joints with uniform microstructures containing continuous reaction layers at both interfaces were only produced by brazing for short periods of time using a T_p close to the liquidus temperature of the ABA. For this particular joint, the formation of overly developed interfaces with a broken Ti₃Cu₃O layer, or fracture of the Fe₂Ti layer and separation of this layer from the Kovar® can be avoided by using a T_p between 820 and 830 °C and τ between 2 and 8 min.

Acknowledgements
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References
335.
[27] H. Okamoto, Supplemental literature review of binary phase diagrams: Au-Ce, B-Pr, Bi-Gd, Bi-Ho, Cd-Sr, Ga-Ti, Gd-Pb, Gd-Ti, Mg-Mn, Mn-Nd, Nd-Ni, and Ni-Ti, J. Phase Equilibria Diffus. 36 (2015), pp. 390–401.
**Figure Captions**

Figure 1. BSEIs of cross-sections of 95 wt.% Al<sub>2</sub>O<sub>3</sub>/Cusil ABA<sup>®</sup>/Kovar<sup>®</sup> joints that were held at 815 °C for a) 0 min, b) 1 min, c) 10 min and d) 15 min.

Figure 2. BSEIs of cross-sections of 95 wt.% Al<sub>2</sub>O<sub>3</sub>/Cusil ABA<sup>®</sup>/Kovar<sup>®</sup> joints that were held at 815 °C for a) 30 min and b) 45 min.

Figure 3. a) TEM bright field image capturing a region of Cusil ABA<sup>®</sup>/Kovar<sup>®</sup> interface in a joint which was held at 815 °C for 15 min, along with electron diffraction patterns from Fe<sub>2</sub>Si with the zone axes b) [2110], c) [5410] and d) [1100]; 00{l} reflections, where \( l \neq 2n \), appear in 3b) and 3c) by double diffraction.

Figure 4. a) Annular dark-field image capturing a small area of the ABA/Kovar<sup>®</sup> interface formed in a 95 wt.% Al<sub>2</sub>O<sub>3</sub>/Cusil ABA<sup>®</sup>/Kovar<sup>®</sup> joint that was brazed for 2 min at 845 °C, along with b–g) EDS maps showing the distribution of several elements in the interfacial phases; stacking faults in the Fe<sub>2</sub>Si particles appear as striations. Electron diffraction patterns from \( \alpha \)-Ti particles, located inside the Fe<sub>2</sub>Si layer, with the zone axes h) [1213] and i) [2423] are shown schematically to identify the relevant reflections clearly.

Figure 5. Electron diffraction patterns from FeSi with the zone axes a) [111], b) [311] and c) [100].

Figure 6. a) TEM bright field image of a Ni<sub>3</sub>Si particle in a joint which was held at 815 °C for 15 min, along with electron diffraction patterns with the zone axes b) [2110] and c) [4223]. A schematic diagram of 6b) is given to indicate the positions of reflections appearing with very low intensity. Streaking in 6b) is a consequence of faulting on the \{0001\} planes.

Figure 7. Electron diffraction patterns from a CuNiTi particle found next to the Fe<sub>2</sub>Si layer in a 95 wt.% Al<sub>2</sub>O<sub>3</sub>/Cusil ABA<sup>®</sup>/Kovar<sup>®</sup> joint, which was brazed for 2 min at 845 °C, with the zone axes a) [031], b) [331] and c) [111].

Figure 8. Electron diffraction patterns from Ti<sub>3</sub>Cu<sub>3</sub>O with the zone axes a) [311], b) [100] and c) [110].

Figure 9. a) Annular dark-field image capturing a small area of the ABA/Al<sub>2</sub>O<sub>3</sub> interface formed in a 95 wt.% Al<sub>2</sub>O<sub>3</sub>/Cusil ABA<sup>®</sup>/Kovar<sup>®</sup> joint that was brazed for 1
min at 815 °C, along with b–g) EDS maps of a α-Ti particle located in the Ti₃Cu₃O reaction layer. Electron diffraction patterns from a γ-TiO particle, located between the Ti₃Cu₃O layer and the Al₂O₃, with the zone axes h) [100] and i) [110] are given.

Figure 10. Thicknesses of the a) FeTi and b) Fe₂Ti layers formed in 95 wt.% Al₂O₃/Cusil ABA®/Kovar® joints which were brazed at a T_p between 815 and 900 °C for 0 to 45 min.

Figure 11. BSEIs of cross-sections of 95 wt.% Al₂O₃/Cusil ABA®/Kovar® joints that were held at 845 °C for a) 2 min, b) 10 min, c) 15 min and d) 45 min.

Figure 12. BSEIs of cross-sections of 99.7 wt.% Al₂O₃/Cusil ABA®/Kovar® joints which were held at 845 °C for a) 2 min, b) 15 min, c) 30 min and d) 45 min, capturing specifically areas of joints having developed interfacial phases at the ABA/Al₂O₃ interface.

Figure 13. Fe–Ni–Ti isothermal section at 800 °C reproduced from [24].

Figure 14. Schematic mechanism for the evolution of the interfacial phases in a 95 wt.% Al₂O₃/Cusil ABA®/Kovar® joint; the Al₂O₃ contains silicon and calcium oxides as secondary phases. Dashed arrows are used to indicate the diffusion of chemical elements and solid arrows are used to label phases. Further details are explained in section 4.1.
Table 1. Chemical composition of the 95 wt.% and 99.7 wt.% Al$_2$O$_3$ components used in wt.%. Average values from 30 electron microprobe measurements with errors of ± one standard deviation are reported. *The quantities of these elements were below or approximately equal to the detection limit.

<table>
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<tr>
<th>Al$_2$O$_3$ purity/ wt.% Al$_2$O$_3$</th>
<th>Al</th>
<th>O</th>
<th>Si</th>
<th>Na</th>
<th>Mg</th>
<th>Ca</th>
<th>Fe</th>
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<td>99.7</td>
<td>55.4</td>
<td>44.0</td>
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Table 2. $T_p$ and $\tau$ used to braze 95 and 99.7 wt.% Al$_2$O$_3$.

<table>
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<tr>
<th></th>
<th>815 °C</th>
<th>845 °C</th>
<th>875 °C</th>
<th>900 °C</th>
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<tr>
<td>0 min</td>
<td>95 wt.%</td>
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<td>–</td>
<td>–</td>
</tr>
<tr>
<td>1 min</td>
<td>95 wt.%</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>2 min</td>
<td>95 and 99.7 wt.%</td>
<td>95 and 99.7 wt.%</td>
<td>95 and 99.7 wt.%</td>
<td>95 wt.%</td>
</tr>
<tr>
<td>6 min</td>
<td>95 wt.%</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>10 min</td>
<td>95 and 99.7 wt.%</td>
<td>95 and 99.7 wt.%</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>15 min</td>
<td>95 and 99.7 wt.%</td>
<td>95 and 99.7 wt.%</td>
<td>95 and 99.7 wt.%</td>
<td>–</td>
</tr>
<tr>
<td>30 min</td>
<td>95 and 99.7 wt.%</td>
<td>95 and 99.7 wt.%</td>
<td>95 wt.%</td>
<td>–</td>
</tr>
<tr>
<td>45 min</td>
<td>95 and 99.7 wt.%</td>
<td>95 and 99.7 wt.%</td>
<td>95 wt.%</td>
<td>–</td>
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</table>
Table 3. Gibbs free energies of formation at 1100 K for TiO and various Si–Ti compounds [28] (data for SiTi₃ and Si₄Ti₅ is unavailable).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔG/ kJ mol⁻¹ Ti</th>
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<tr>
<td>Ti + $\frac{1}{2}$O₂ → TiO</td>
<td>−437</td>
</tr>
<tr>
<td>Si + Ti → SiTi</td>
<td>−129</td>
</tr>
<tr>
<td>2 Si + Ti → Si₂Ti</td>
<td>−127</td>
</tr>
<tr>
<td>$\frac{3}{5}$Si + Ti → $\frac{1}{5}$Si₃Ti₅</td>
<td>−118</td>
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</table>
Figure 1. BSEIs of cross-sections of 95 wt.% $\text{Al}_2\text{O}_3$/Cusil ABA®/Kovar® joints that were held at 815 °C for a) 0 min, b) 1 min, c) 10 min and d) 15 min.
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