Joining of Powder Metallurgy Beta Gamma Titanium Aluminide through Diffusion Brazing

by

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The undersigned hereby recommends to the
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acceptance of the dissertation

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Abstract

This thesis presents an experimental study of diffusion brazing powder metallurgy beta gamma titanium aluminide, along with a methodology utilizing pentenary equivalent beta forming effectiveness for the design of post bond heat treatments. Beta gamma titanium aluminides are attractive high temperature materials with low density and high specific strength. Adequate joining and repair methods, and the resultant high temperature creep performance, are fundamental requirements for the adoption of beta gamma titanium aluminides in the aerospace, automotive, and land based gas turbine industries. The developed beta forming effectiveness methodology was utilized to target composition and post bond heat treatment parameters to achieve a fully lamellar microstructure. Experimental results indicate that diffusion brazing beta gamma alloy below the eutectoid temperature of the substrate results in an α_2 reaction layer at the solid/liquid interface that retards diffusion of the melting point depressant. When the brazing temperature is raised above the eutectoid temperature, the kinetics are enhanced due to the formation of a disordered α phase at the solid/liquid interface resulting in complete solidification at low holding times. A step cooled post bond solutionizing heat treatment produces a fine near fully lamellar microstructure within the bond zone. Aging of the solutionized microstructure manifests interfacial $\beta_{0,sec}$ precipitates within the bond zone and parent material lamellar colonies. Intercolony β_0 phase regions experience the precipitation of two previously unreported phases which do not significantly alter the microhardness across the bond zone. Creep tests conducted on the parent material reveal improved primary creep resistance and reduced rupture time with aging. Creep tests conducted on the post bond heat treated specimens reveal that high stress levels result in premature rupture due to bond-line porosity acting as sites for void coalescence. Decomposition of the intercolony β_0 phase occurred during creep due to the altered composition and hence ω solvus temperature within the bond zone. With proper management of bond-line porosity, diffusion brazing meets or exceeds the performance of the parent material

in the primary creep regime at low stress levels.

To Leili and Evan.

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Chapter 1

Introduction

1.1 Motivation

Gamma titanium aluminide (γ -TiAl) alloys exhibit an excellent combination of density, strength, oxidation resistance, and creep properties at elevated temperature when compared with nickel-based superalloys [1]. However, conventional γ -TiAl alloys have seen limited use due to a small processing window, and lack of balance between room temperature strength/ductility and high temperature fracture/creep resistance [1–3]. The room temperature ductility for conventional γ -TiAl is shown in Figure 1.1 and indicates the relatively low ductility range of 0.2-2.5% with high sensitivity to composition and microstructure. Processing such intermetallics with this sensitivity to ductility and microstructure has proven a challenge [2].

From an application standpoint, TiAl alloys are of interest primarily to the aerospace, automotive, and land-based industrial gas turbine industries. Within the aerospace industry, hot section gas turbine engine components made from heavier nickel based superalloys are primary candidates for replacement with titanium aluminides. By replacing heavier nickel based super alloy components with titanium aluminides, a significant weight savings can be achieved allowing further optimized weight savings throughout the design of the aircraft. Such optimization in design leads to improved fuel efficiency and reduced carbon emissions. Examples of candidate components include low-pressure turbine (LPT) blades, high-pressure turbine (HPT) blades, stator vanes, exhaust components, combustor casings, diffusers, and dampers.

Within the automotive industry, a similar motivation in the improvement of fuel

Figure 1.1: Room temperature ductility of binary TiAl at various aluminum concentrations [3].

economy and reduced emissions has led to the adoption of titanium aluminides. By attempting to reduce the size of the internal combustion engine while maintaining performance and efficiency, an increase in the combustion temperature has led to the development of titanium aluminides for engine valves, turbocharger wheels, and connecting rods.

Land based gas turbines are currently experiencing growth due to an increased demand for higher efficiency combined cycle gas turbine power-plants [4]. Improvements in the power output, and thus efficiency, of land based gas turbine engines have been achieved through increased inlet temperatures resulting from improved cooling systems used to maintain blade integrity. Additionally, single crystal nickel based superalloys that can handle higher operating temperatures, have been incorporated into land based applications towards improving efficiency [5]. Increasing blade length is also an option for increasing power output at the expense of stress at the root of the blade. Specifically, the centrifugal stress in the blade depends on the rotational speed, blade material, and length of the blade [6]. This stress is directly proportional to the density of the material and the square of the hub-tip ratio. Thus, replacing nickel based superalloys with light weight TiAl offers a means to increase blade length without increasing stress at the root of the blade. However, implementing this strategy may require welding or brazing methods for component attachment, as well as for repair of casting defects prior to blade introduction.

From a processing point of view, functional TiAl turbine blade investment castings are difficult to produce in length greater than a few centimeters due to extensive porosity, hot-tear, segregation, and the formation of large α grains resulting in long lamellae [1, 2, 7]. However, these technological barriers have been more recently overcome with the adoption of LPT blades made from titanium aluminides in the latest General Electric Genx-1B engine. To overcome the technological challenges associated with casting LTP TiAl blades, it is believed that these blades were cast oversized and then machined to their final dimensions [8].

To overcome the processing challenges associated with γ -TiAl, early introduction of the β phase into the microstructure has shown significant promise for improved hot forging and machining [9, 10]. However, the potential improvements in processing are realized at the expense of lower strength at elevated temperature when compared with γ -TiAl [11]. Figure 1.2 compares the yield strength versus operating temperature for a number of different alloy systems. Beta gamma TiAl alloys have similar yield strength performance to conventional γ -TiAl at temperatures ranging from 660 °C to 850 °C [12]. However, increasing temperature above 850 °C results in a drop in yield strength due to significant softening of the β phase [13]. Therefore, beta gamma TiAl with a significant volume fraction of the β phase may not replace γ -TiAl or nickel based superalloys at temperatures greater than 850 °C. However, beta gamma TiAl may be considered a more economical alternative for use at intermediate operating temperatures if a processing route that produces a consistent, stable, and attractive microstructure can be achieved.

In addition to the processing challenges and inherent low ductility of TiAl alloys, the joining and repair potential of advanced materials such as beta-gamma TiAl is a critical parameter to the successful adoption of novel materials on an industrial scale. Generally speaking, the mechanical properties associated with joined or repaired material must approach that of the parent material in order to be considered a viable material option [14]. Conventional γ -TiAl has seen success when joined using transient liquid phase bonding/diffusion brazing (TLPB/DB) with post bond heat treatments (PBHT) achieving tensile and bend strengths similar to that of the parent material under identical thermal conditions [15]. However, the creep resistance of such bonds has generally not been reported, and is a critical factor in determining the potential for bonding and repair of gas turbine rotating components [16].

Figure 1.2: Yield strength versus temperature for various alloy systems [11].

1.2 Objectives & Outline

Improving the room temperature ductility of TiAl, while providing a joining and repair route, will improve the affordability of TiAl intermetallics. The use of conventional forming and joining methods increases flexibility in processing and leads to a greater adoption of TiAl material. Greater adoption by both the aerospace and land based gas turbine industries further results in improved efficiency of aircraft due to lighter weight components, reduced carbon emissions, and reduced stress on support structures. However, adoption of a new TiAl material such as beta gamma TiAl, requires an understanding of the effect of prolonged high temperature service on the microstructural stability and mechanical properties of the material. Demanding applications such as high temperature vanes, blades, and blisks may place strict requirements on variability in mechanical properties over the operational life of a component. Minimizing microstructure and property changes will further assist with adoption of beta gamma TiAl.

The research objectives for this thesis include;

1. The evaluation of P/M beta gamma alloy creep response at elevated temperature
2. Determine a diffusion brazing interlayer and thermal cycle that produces a

near fully lamellar microstructure across the bondline with similar colony size, lamellar spacing, interfacial precipitates, and colony boundary morphology as the unaffected parent material.

3. Elucidate the mechanisms that control the resultant microstructural response as a result of the diffusion brazing process for P/M beta gamma titanium aluminides.
4. Determine the effect of the diffusion brazing process on elevated temperature creep response of P/M beta gamma titanium aluminides. Elucidate the mechanisms that control the creep response as related to the diffusion brazing process for P/M beta gamma titanium aluminides.

A literature review is provided in Chapter 2 and consists of the the latest developments in the understanding of beta solidified titanium aluminide microstructures and heat treatment processing routes, and their impact on elevated temperature creep performance. Additionally, a review of the transient liquid phase bonding / diffusion brazing technique as applied to conventional and experimental titanium aluminides is conducted. A review of the theory associated with the diffusion brazing process as it applies to both solid solution mult-component alloys and intermetallic alloys is provided. Chapter 3 details the materials utilized as part of this thesis, the experimental methods, diffusion brazing and post bond heat treatment test plan, and the the microstructural and mechanical characterization techniques that were carried out. Chapter 4 details the as-bonded microstructural response both within the braze zone and on the parent material along with the associated kinetic mechanisms that drive the diffusion brazing response for beta gamma alloys. Chapter 5 details the post bond heat treatment design objectives as well as the resulting microstructures that were achieved through solutionizing and ageing heat treatments. Chapter 6 details the elevated temperature creep response for both the P/M beta gamma alloy virgin material as well as the optimized diffusion brazed / post bond heat treated condition at both low and intermediate stress levels. The final chapter summarizes the significant contributions and observations made, and suggests possible future research.

Chapter 2

Literature Review

2.1 Crystal Structure

Intermetallics are compounds of two or more metals with crystal structures that differ from the constituent elements. Intermetallic compounds exist in a number of different lattice structures. The ordering of these structures, both short-range and long-range may have a significant effect on the physical and mechanical properties of the material both at room temperature and at elevated temperature. For titanium aluminide alloys, a focus in the literature on three primary phases has been undertaken due to the unique and rich combination of microstructures and hence mechanical properties that may be realized through various processing routes. Those phases consist of the ordered face centered tetragonal γ -TiAl phase, the ordered hexagonal α_2 -Ti₃Al phase, and the ordered/disordered BCC B2/ β phase (Figure 2.1).

A unique aspect of the β phase is that it may exist as both an ordered phase

Figure 2.1: Crystal structures associated with modern titanium aluminide engineering materials, (a) Ti₃Al, (b) TiAl, (c) B/B2 [8].

β_2 /(B2) (CsCl) or disordered (A2-BCC) phase depending on temperature (i.e. disordered above 1000-1200 °C [17]) and provides a sufficient number of independent slip systems to improve deformability at elevated temperature by hindering the growth of microcracks that form in the more brittle α_2 and γ phases [18,19]. Additionally, the presence of the β phase at elevated temperatures acts as a lubricating layer for other phases during deformation [13]. It is the inherent properties of the disordered BCC β crystal structure that provides additional flexibility in processing TiAl. However, this additional flexibility in processing comes at the detriment to in-service mechanical properties if the β phase is not minimized from the microstructure prior to placing hot section components in-service. Thus the processing route utilized to manufacture titanium aluminide alloys is a critical factor in the end-use/long term performance of these materials.

2.2 Composition, Microstructures, and Phase Transformations

2.2.1 Conventional γ -TiAl

Conventional γ -TiAl alloys typically consist of an aluminum composition ranging from 45-50 at.% with various alloying elements added in small quantities to achieve desired microstructural features and hence mechanical properties. Common microstructures for conventional γ -TiAl consist of two phase $\gamma + \alpha_2$ mixtures in one of four microstructural forms [20] (i.e. fully lamellar, near-lamellar, duplex, and near- γ , Figure 2.2). These four microstructures are achieved when processed at various temperatures associated with the associated equilibrium phase diagram (Figure 2.3). Both the γ and α_2 phases have limited ductility at room temperature due to their long range atomic order and hence reduction of slip systems [18]. This however has not precluded these alloys from extensive research and recent adoption into next generation gas turbine engines when composition and processing conditions are well controlled.

Figure 2.2: Various conventional γ -TiAl microstructures. (a) Duplex, (b) Near Gamma, (c) Near Lamellar, (d) Fully Lamellar. [20]

Figure 2.3: Binary Ti-Al phase diagram with heat treatment temperatures used to develop the various microstructures in conventional γ -TiAl: FL: fully lamellar, NL: near lamellar, D: duplex, NG: near gamma [21].

2.2.2 Beta Solidified TiAl and Beta Gamma Alloy

Beta solidifying titanium aluminides, as the name suggests, solidify through the beta phase as opposed to the more conventional alpha phase (peritectic) solidification pathway for conventional γ -TiAl (Figure 2.4). The suggested advantage in beta solidification over alpha (peritectic) solidification is the potential for grain refinement, a reduction in casting texture that occurs due to crystal partitioning [8], and reduced segregation during cooling [19].

During peritectic solidification of binary γ -TiAl alloys with compositions ranging from 45-49 at.%Al, the disordered β phase is the primary phase that forms. However the α phase generally grows simultaneously within the melt due to direct solidification of the peritectic reaction and not by direct interaction between the melt and the primary β phase [8]. As solidification continues, the peritectoid line at 1491 °C is reached and a two-phase $\alpha + \beta$ structure is realized. The α structure during the liquid to solid transformation grows preferentially along the c-axis of the h.c.p. crystal structure in the direction of heat extraction. On further cooling, each phase within the two-phase $\alpha + \beta$ structure undergoes different transformations. The existing α

Figure 2.4: Central portion of the binary Ti-Al phase diagram. Left of the arrow, solidification occurs through the β phase while right of the arrow solidification occurs through the peritectic reaction [22].

phase will transform to a two phase $\alpha_2 + \gamma$ lamellar structure, while the β phase will transform to α with an orientation dependent on the pre-existing α phase from the peritectic reaction. It is this pre-existing orientation that limits the potential number of slip systems and hence limits the ductility of conventional γ -TiAl alloys.

In order for beta solidification to occur, the composition is generally depressed in aluminum content at the expense of beta stabilizing elements. The solidification pathway is shifted to lower Al content, potentially avoiding the peritectic reaction and maintaining a portion of the structure as the β phase throughout a significant portion of solidification process. For binary intermetallic TiAl alloys, the beta solidification process occurs when the aluminum content in the liquid remains below approximately 45 at.% as shown in Figure 2.4, resulting in the suppression of the $L \rightarrow L + \beta \rightarrow \alpha$ peritectic reaction. By ensuring the Al content within the liquid remains below 45 at.% during solidification, the transformation from the liquid phase will follow the $L \rightarrow L + \beta \rightarrow \beta$ pathway, which favors the realization of numerous orientation variants in α grains during the $\beta \rightarrow \alpha$ solid-state transformation [19, 23, 24]. If the liquid concentration increases above 45 at.%, solidification may occur through

the peritectic $L \rightarrow L + \beta \rightarrow \alpha$ pathway that may result in significant chemical inhomogeneities leading to segregation and a deterioration of mechanical properties [3]. By solidifying completely through the β phase, the peritectic reaction may be minimized, and the manifestation of the β phase can take place with only slight microsegregation [19]. Depending on the solidification conditions, the formation of a thin peritectic layer may occur on cooling and may cause interdendritic segregation to occur. Therefore, ensuring a process that can achieve the desired phase fractions is important when processing TiAl alloys for specific mechanical properties, which is why powder metallurgical processing based on rapidly quenched gas atomized powders has become a potential method to overcome such conventional casting concerns.

2.2.3 Composition

Beta solidifying γ -TiAl alloys have been concurrently investigated by a number of different research groups over the past 10+ years [8, 10, 13, 24–27]. As such, different research groups classify the microstructure based on the equilibrium phase diagrams according to the constitution of the specific alloy under investigation. A number of specific alloys have emerged as providing a potential balance between room temperature ductility and high temperature mechanical performance. A brief description of selected emerging alloys is described.

Beta solidified titanium aluminide alloys with Nb and Mo additions termed “TNM” alloys have a nominal composition of Ti-43.5Al-4Nb-1Mo-0.1B (at.%), while TNB alloys are considered a high Nb bearing TiAl alloy with a nominal composition of Ti-(42–45)Al-(5–10)Nb-(0–0.5B) (at.%) when taken through a beta solidification process [19]. Variants of both the TNM and TNB alloys have been investigated to improve on their stability and mechanical performance at both room temperature and elevated temperature. For TNM alloys, the resultant microstructures consist of near lamellar γ (NL- γ), duplex structure (DP), near lamellar beta (NL- β), and fully lamellar (FL) microstructures [28]. A selection of microstructures for TNM alloy is shown in Figure 2.5. Significant effort has been undertaken to experimentally verify the equilibrium phase diagram for the TNM alloy through various in-situ techniques [28, 29]. For the TNM alloy, evaluation of the effect of varying amounts of Nb and Mo within the composition range of interest reveal that the ratio of Nb to Mo has a significant impact on the ability to suppress the equilibrium β phase volume fraction above the eutectoid temperature. Also, the addition of C, B, and Si along with variation in heat

Figure 2.5: Select TNM alloy microstructures. (a) As-cast, (b) Near lamellar gamma (c) Near lamellar beta, (d) Fully Lamellar [28].

treatment following the typical Cast/HIP process have been shown to significantly influence microstructure and hence mechanical properties such as creep response, tensile strength, and elongation at both room temperature and elevated temperature. Much research has been performed on TNB alloys with a nominal Al content of 45 at.%. The duplex structure is associated with excellent creep resistance and plastic fracture strains on the order of 2-2.5 .% providing an excellent balance of ductility and performance [8]. The Clemens group has primarily focused on castings as the starting material with follow on HIP'ing, forging, and/or heat treatments to generate various microstructures. Additional powder metallurgy (P/M) research [30, 31], as well as joining trials have also been reported by the research group for beta solidified titanium aluminides [32].

In addition to the work performed by Clemens et al, significant research conducted

Table 2.1: Beta gamma TiAl phase constituents and solidification pathways.

Group	Solidification Pathway
A	$L \rightarrow L + \beta \rightarrow \beta \rightarrow \alpha + \beta \rightarrow \alpha \rightarrow \alpha + \gamma \rightarrow \gamma \rightarrow \alpha_2 + \gamma$
B	$L \rightarrow L + \beta \rightarrow \beta \rightarrow \alpha + \beta \rightarrow \alpha + \beta + \gamma \rightarrow \alpha_2 + \gamma + \beta_2$
C	$L \rightarrow L + \beta \rightarrow \beta \rightarrow \alpha + \beta \rightarrow \alpha + \gamma + \beta \rightarrow \beta_2 + \gamma$

on ternary Ti-Al-M alloys containing high Nb/Mo/V/Mn constituents has been carried out by Takeyama et al [9, 10, 33–36]. The work performed by Takeyama et al has contributed significant insights into the equilibrium phase diagrams for ternary compositions depleted in Al and enriched in a number of beta stabilizing elements. Additionally, variation in constitution, heat treatments, and forging parameters has led to significant improvements in hot forgeability, machinability, and creep resistance of the associated ternary alloys.

Alternatively, in 2006, the term “Beta Gamma TiAl” was supposedly first coined by Y-W. Kim, S-L. Kim, D. Dimiduk, and C. Woodward at the 3rd International Workshop on Gamma-TiAl Technologies held in Bamberg, Germany from May 29–31, 2006 [37]. As defined by Y.-W. Kim, beta gamma TiAl (beta-gamma alloy) is a multi-component intermetallic alloy with a nominal composition range of Ti-(40-45)Al-(2-8)Nb-(1-9)(Cr, Mn, V, Mo)-(0-0.5)(B, C) atomic percent (at.%). Beta gamma TiAl have been categorized by Y.W Kim into three different groups depending on the final equilibrium phase distribution obtained through the beta solidification process. The three alloy groups and their transformation pathway are listed in Table 2.1, and shown in Figure 2.6. The quasi-isopleth phase diagram (Figure 2.6) is based on the Ti-44Al-x M_{eff} ternary phase diagram where M_{eff} is the effective β stabilizing composition utilized in the alloy. The alloy groups are characterized by the presence of specific phases below the eutectoid temperature. Group A alloys form a two phase $\alpha_2 + \gamma$ structure, group B alloys contain a three phase mixture consisting of $\alpha_2 + \gamma + \beta_2$, and group C alloys contain a two phase mixture consisting of $\beta_2 + \gamma$ phases. Efforts have been made to verify the proposed quasi-isopleth phase diagram through thermodynamic modeling [38]. The results of which have shown relatively good agreement, although suppression of a single α phase field for group B alloys may be highly dependent on the selected alloying elements and associated quantities

Figure 2.6: Quasi-Isopleth of the Ti-44Al-xM ternary phase diagram indicating the three alloy groups for beta gamma TiAl [39].

within the alloy under investigation.

Solidifying through the group “A” pathway has shown to produce a fully lamellar as-cast microstructure consisting of two phase ($\gamma + \alpha_2$) colonies with the addition of approximately 1.5 vol.% β phase as shown in Figure 2.7a when beta solidified to the two phase $\alpha + \beta$ phase field followed by quenching. Further hot isostatic pressing (HIP’ing) this alloy produces a near lamellar microstructure with approximately 2.0 vol.% β phase present in the microstructure (Figure 2.7b) . Group A specimens produced through a HIP’d P/M route exhibit a fine triplex structure with a volume fraction of β phase of approximately 1.0% [40, 41].

For group B alloys, significant increase in β phase volume fraction at room temperature has been achieved. Additional beta stabilizing elements have the beneficial effect of extending the beta phase field to higher aluminum content where room temperature ductility is higher. As-cast microstructures consist of a near lamellar three phase structure ($\gamma + \alpha_2 + \beta$) containing 14 vol.% β phase. In addition, consolidating gas atomized powders of the group B alloy followed by HIP’ing produces a near- γ three phase ($\gamma + \alpha_2 + \beta$) structure containing approximately 9.4 vol.% β phase as

Figure 2.7: Various beta gamma TiAl microstructures. (a) Group A, as cast [39], (b) Group A, as-cast and HIP'd [39], (c) Group B, as-cast and HIP'd [39], (d) Group B, P/M HIP'd [41].

Figure 2.8: Select Group C beta gamma TiAl microstructures for a Ti-43Al-5V-4Nb (at.%) forged alloy [42]

shown in Figure 2.7d.

Group C alloys have greater beta stabilizing elemental composition compared to the Group A, or Group B/TNM alloys. High Nb bearing alloys fall within the Group C category (analogous to TNB alloys) which has been a major focus for a number of research groups due to their enhanced hot workability at near conventional forging temperatures. Examples of Group C alloy microstructures are shown (Figure 2.8) and are classified into two main categories; (1) near lamellar (NL), and (2) triplex (TP) microstructures. NL microstructures are obtained in Group C alloys when processed in the two $\alpha + \beta$ phase field followed by quick cooling to the $\beta_2 + \gamma$ phase field. TP structures are obtained when processed in the triple $\alpha + \beta + \gamma$ phase field.

2.2.4 Solution Heat Treatment

Under high temperature operating conditions in the 700-850 °C range, typical of gas turbine components, the presence of the β phase in significant volume fraction greater than 10 vol.% is detrimental to strength and creep resistance [9,10,33]. Efforts

have been made to remove the β phase during final processing to improve on high temperature performance [40, 43]. In order to achieve adequate high temperature creep performance, the purpose of the solutionizing heat treatment is to transform the high β volume fraction microstructure to a fully lamellar two phase ($\alpha_2 + \gamma$) structure with a fine colony size, fine lamellar spacing, well interlocked colony boundaries, with β phase volume fractions reduced to less than 3 vol%, similar to conventional fully lamellar γ -TiAl.

Different approaches have been taken to investigate the influence of heat treatments on resultant microstructure and mechanical properties of beta gamma titanium aluminides. The first approach incorporates a typical single-step solutionizing heat treatment (Figure 2.9, Heat Treatment #1). In this type of heat treatment, the temperature, time and cooling rate from the solutionizing temperature are varied to understand the impact on forming various microstructures from the associated equilibrium regions. A second approach is to incorporate a two-step heat treatment whereby heat treatment #1 is combined with heat treatment #2 in Figure 2.9. A third approach is termed “step cooled solution heat treatment (SCHT)” (Heat Treatment # 3 in Figure 2.9), whereby instead of conducting two separate heat treatments, the cooling rate from the solutionizing temperature to a prescribed lower temperature is kept low (i.e. furnace cooling or controlled cooling on the order of 10 K/min) followed by a transition to quick air cooling to room temperature. Thus a further critical parameter of importance in this heat treatment strategy is the transition from furnace cooling to air cooling (i.e. the $T_{F/A}$ temperature).

In the first approach, the solutionizing temperature is commonly performed in one of three regions associated with the equilibrium phase diagram. The three main regions are; (1) the single β phase region, (2) the two phase $\alpha + \beta$ region, or (3) the three phase $\alpha + \gamma + \beta$ three phase region (i.e. when this region exists). Depending on the constitution of the alloy, a single phase α phase region may also exist (i.e. Group A alloys as depicted in Figure 2.9, and possibly group B alloys), and is generally avoided due to the lack of a second phase that acts to restrict alpha phase grain growth. Holding time at temperature and cooling rate will dictate the evolution and resultant volume fraction of the various three phase constituents within the microstructure. Air cooling from the various equilibrium regions in the β and $\alpha + \beta$ phase field will transform a large fraction of β grains to α grains, and subsequently transform the the resultant α grains to a metastable lamellar α_2/γ structure, while retaining β phase at

Figure 2.9: Quasi-Isopleth of the Ti-44Al-xM ternary phase diagram superimposed with single-step, dual-step and step-cooled heat treatment options for beta gamma TiAl.

colony boundaries. For a single-step solutionizing temperature within the three phase $\alpha + \beta + \gamma$ phase field, equiaxed γ grains will also form, and the lamellar colony volume fraction will be reduced resulting in a triplex structure of lamellar colonies, equiaxed γ grains, and equiaxed β grains. Slow cooling from the solutionizing temperature will also promote the formation of a triplex structure depending on the length of time spent traversing the three phase $\alpha + \beta + \gamma$ phase field.

In the second two-step approach, the first heat treatment is generally conducted in the single β phase field or high in the two phase $\alpha + \beta$ phase field to promote lamellar colony formation on air cooling. While the second heat treatment is performed just above the gamma solvus temperature to further minimize the β phase within the microstructure before cooling. Quick cooling from just above the gamma solvus temperature will suppress the formation of globular γ grains. Such a two step solutionizing treatment has been shown to improve lamellar colony volume fraction by slightly reducing the β phase seam width at colony boundaries, and promoting a fine fully lamellar microstructure with significant meta-stable α_2 lath volume fraction [28].

In the third approach, the material is rapidly heated into the single β phase field or high in the $\alpha + \beta$ phase field and held for a sufficient length of time to promote

homogenization of the alloying elements. Beta stabilizing elements such as Mo and Nb, with their relatively low diffusivities require high temperature and significant holding time to promote solute redistribution [44]. The material is then slowly cooled to a temperature just above the $\gamma + \alpha + \beta$ phase field where the volume fraction of β phase is minimized [29]. Slow furnace cooling from the solution heat treatment temperature promotes the reduction of the β phase, but holding the alloy at such high temperatures may contribute to grain growth. Therefore, achieving equilibrium conditions as quickly as possible just above the $\alpha + \beta \rightarrow \alpha + \beta + \gamma$ transus from a homogenized state minimizes both the existence of the β phase and α grain growth. From a temperature just above the $\alpha + \beta + \gamma$ phase field, beta gamma TiAl alloys have been shown to contain anywhere from 76-93 vol.% $\alpha + \gamma$ phase with the remainder as β phase depending on composition [29]. A quick air cool to room temperature from the $T_{F/A}$ temperature avoids the formation of γ grains while traversing the $\alpha + \gamma + \beta$ phase field, and promotes the formation of the high volume fraction of the α phase to a fully lamellar $\alpha_2 + \gamma$ microstructure. However, if the cooling rate is too fast, massively transformed gamma grains, γ_M , may occur at α grain boundaries suppressing the $\alpha \rightarrow \alpha_2 + \gamma$ fully lamellar transformation which is dependent on the constitution of the alloy [45]. Since group B/C alloys must traverse the $\alpha + \gamma + \beta$ phase field, some β phase will be retained in the microstructure. However, the minimization of the β phase is achieved through quick air cooling through the $\alpha + \gamma + \beta$ phase field below the eutectoid temperature which promotes the formation of fine lamellae known to improve high temperature creep resistance [46].

Group B beta gamma TiAl microstructures taken through a SHT heat treatment have been reported [40]. These group B solution heat treated microstructures exhibit fully lamellar colonies with lamellar spacings on the order of $0.04 \mu\text{m}$ and colony sizes on the order of $40 \mu\text{m}$. The microstructure of a group B alloy in the SHT condition is shown in Figure 2.10. The β phase manifests itself as fine particles along the colony boundaries with a volume fraction less than 1.0%. During solution heat treatment, composition plays an important role in the resultant microstructure. Boron additions have been found to increase the rate of heterogeneous α phase grain nucleation during the $\beta \rightarrow \alpha$ transformation. Also, by increasing the Nb and Mo content at the expense of the Al content, a decrease in the linear grain growth rate is achieved due to low diffusion mobility in the γ and α_2 phases [23, 47].

Figure 2.10: P/M beta gamma TiAl Group B microstructures after SCHAT, optical micrograph (right), SEM grain boundary morphology (center), and SEM lamellar morphology (left) [40].

Group C microstructures associated with a step-cooled solutionizing heat treatment have also been reported [35,48]. As an example, a high Nb bearing Ti-45Al-10Nb (at.%) alloy in the as-cast condition was subjected to a solutionizing heat treatment of 1400 °C for 5 hours followed by furnace cooling to 1000 °C followed by air cooling. The microstructure associated with this solutionizing heat treatment is fully lamellar with no Nb segregation, no retained β_0 phase, a colony size on the order of 150 μm , with a well interlocked serrated colony boundary morphology (Figure 2.11). Additionally, Takeyama et al. [35], experimentally generated a TTT diagram for a Ti-42Al-8V (at.%) group C alloy (Figure 2.12), and demonstrated the combined transformation pathway of a SCHAT heat treatment for slow cooling from the solutionizing temperature followed by controlled cooling from the $T_{F/A}$ temperature. In that work, the slow cooling from the solutionizing temperature transforms the high temperature β phase to α phase. Once the α phase finish transformation time (α_f) is reached, the cooling rate is increased to avoid excessive α grain growth, and further controlled cooling at a higher cooling rate results in the near lamellar transformation by avoiding the secondary β phase start curve (β_s).

Figure 2.11: Resultant microstructure of a Group C alloy (Ti-45Al-10Nb (at.%)) subjected to a step cooled solution heat treatment of 1400 °C for 5 hours followed by furnace cooling to 1000 °C followed by air cooling to room temperature [48].

Figure 2.12: TTT diagram for a Ti-42Al-8V (at.%) alloy indicating the phase transformation kinetics for a SCHT of 1473K $\rightarrow$ 1423 K at 0.4 K/min + controlled cooling from 1423 K $\rightarrow$ 1023 K at 10 K/min followed by WQ. [35]

2.2.5 Aging Heat Treatment

Aging treatments are carried out to stabilize the microstructure, and to generate interfacial precipitates at the lamellar interfaces. Stabilization of the microstructure is important as the meta-stable nature of the fine fully lamellar microstructure will decompose towards an equilibrium globular type microstructure caused by a breakdown of the lath structure due to longitudinal and/or lateral dissolution of the metastable α_2 laths towards the equilibrium phase fractions. Additionally, cellular reactions may occur at lamellar colony boundaries forming equiaxed $\beta + \gamma$ grains causing a breakdown of the serrated colony boundary character that is known to enhance creep resistance due to the well interlocked structure. Further to these two decomposition effects, decomposition of the intercolony β phase may occur for high Nb bearing beta gamma alloys via the transformation of the ordered β_0 phase to a $\text{Ti}_4\text{Al}_3\text{Nb}$ compound (ω_0) phase with B8_2 crystal structure (Figure 2.13b). This decomposition reaction is dependent on the composition of the alloy and occurs for alloys with significant Nb content on the order of 4 at.% or greater. For example, the TNM group B alloy with 4 at.% Nb and 1 at.%Mo exhibits the decomposition of the β_0 phase at an isothermal temperature ranging from 750 °C to 825 °C (Figure 2.13a), typical of the operating range for gas turbine components, and the resultant high hardness of the ω_0 phase may lead to embrittlement of the microstructure. Further to Nb bearing alloys, Mo containing TiAl alloys may also exhibit a similar decomposition of the β_0 phase. Thus, the long term stability of beta gamma alloys with beta stabilizing alloying elements in the 700-800 °C temperature range requires further investigation due to the known decomposition effects such as lath dissolution and or the decomposition of the β phase that may alter the microstructure, potentially deteriorating mechanical properties at elevated temperatures [24].

The generation of fine precipitates is a well known method of strengthening titanium aluminides [8]. Typical methods such as adding very small quantities on the order of 0.1-0.5 at.% of C, B, Si, or other light elements to precipitate low solubility compounds with Ti such as carbides, borides, or silicides has proven a common method to improve on the mechanical performance of titanium aluminides. The precipitation of secondary phase particles is also possible given the proper constitution and thermomechanical heat treatment of the alloy. A typical example is the generation and growth of GP zones in commercially available heat treatable aluminum

(a)

(b)

Figure 2.13: (a) Decomposition of the β_0 phase for TNM alloy determined through in-situ HEXRD, (b) resultant BSE-SEM imaging showing fine ω_0 grains within a β_0 intercolony region after heat treating at 780 °C for 300 hours [49]

alloys. As such, the precipitation of an ordered $\beta_{0,sec}$ phase precipitate within gamma titanium aluminide alloys has also been demonstrated through secondary thermomechanical treatments when alloyed with beta stabilizing elements such as Cr, Nb, W, Mo, and Fe [35, 50, 51].

The proper SCHAT heat treatment applied to ternary beta gamma alloys and multicomponent beta gamma alloys produces a metastable lamellar microstructure with significant excess α_2 lath volume fraction. A secondary aging heat treatment below the eutectoid temperature is applied following the SCHAT to nucleate and grow interfacial $\beta_{0,sec}$ phase precipitates (Figure 2.14). The $\beta_{0,sec}$ phase nucleates and grows at the expense of α_2 lath dissolution towards equilibrium and is schematically shown in Figure 2.15. With the proper distribution and morphology, these interfacial precipitates have been shown to improve primary creep resistance by hindering dislocation emission and motion through the γ laths [50, 52, 53]. Specifically, glide dislocations are only retarded from motion when hindered by a fine distribution of precipitates. A fine distribution of precipitates are generated when the prior α_2 lath is thick as opposed to thin. Additionally, lamellar delamination may also be hindered by the interfacial β phase precipitates improving tensile strength [54]. Thus, with the proper thermomechanical heat treatment, a reduction in primary β to a near-fully lamellar microstructure, while initiating the precipitation of secondary beta phase precipitates ($\beta_{0,sec}$) may be exploited to improve on the high temperature creep performance of beta gamma titanium aluminides.

For P/M Ti-xAl-2Nb-2Mo (at.%) beta gamma TiAl, aging treatments have been performed from 800 °C to 950 °C with various holding times ranging from 0-96 hours followed by air cooling to room temperature [40]. A mix of quantitative and qualitative assessments of the various microstructural transformations that occur in beta gamma TiAl have been carried out. Specifically, colony growth and lamellar spacing have been quantitatively measured, while the morphological changes at the colony boundary interfaces, the volume fraction of $\alpha_2 + \gamma$ or β phase, and the rate of $\beta_{0,sec}$ precipitation at the lamellae boundaries have been assessed qualitatively with increasing holding time at various aging temperatures. A micrograph of beta precipitation formation with increased aging time at 900 °C from 0 to 96 hours is shown in Figure 2.16. The $\beta_{0,sec}$ phase morphology is acicular in nature and the time to nucleate these precipitates decreases with increasing aging temperature. The

Figure 2.14: Interfacial beta phase precipitates formed in a Ti-42Al-8V alloy via a secondary heat treatment at 1273K for 900 seconds following a SHT. (a) BSE-SEM, (b) bright field TEM. [35]

Figure 2.15: Schematic interaction of interfacial precipitates with dislocations within the prior lamellar structure. [50].

Figure 2.16: P/M beta gamma TiAl Group B microstructures after SCHT + 0 hours (left), 24 hours (center), and 96 hours (right) aging time at 900 °C [40].

$\beta_{0,sec}$ phase manifests itself due to the excess amount of α_2 phase retained in the solutionized microstructure as a consequence of rapid cooling to achieve the fully lamellar microstructure [50]. Upon further aging, the excess α_2 lamellae decompose towards equilibrium, resulting in an increase in β phase volume fraction. Long term aging up to 800 hours has shown that the decomposition of α_2 lamellae in γ -TiAl with sufficient β stabilizers may result in β phase volume fractions on the order of 15-23% [55]. Additionally, this alloy does not appear to decompose the intercolony β_0 phase to the ω_0 phase when subjected to heat treatments at 800 °C.

2.3 Mechanical Properties

2.3.1 Creep Response

For conventional titanium aluminides, the greatest creep resistance is achieved through a fully lamellar microstructure with fine continuous lamellar size and spacings. Additionally, orientation of the lamellar colonies in relation to the loading axis will play a role in creep resistance, along with the colony boundary morphology and colony size. The fine lamellar spacing reduces the effective slip length for dislocations compared with equiaxed microstructures [8]. Thus, when equiaxed $\beta + \gamma$ grains are located at colony boundaries or within colonies, creep resistance is reduced. Also, since the lamellar spacing is a critical parameter to hindering dislocation motion, the discontinuous coarsening of the lamellar structure will further reduce creep strength.

For titanium aluminides containing fine interfacial beta phase precipitates, creep resistance is improved [50]. This improvement in creep resistance is a result of the interfacial precipitates further hindering the emission and motion of dislocations

Figure 2.17: A Ti-48Al-2W gamma titanium aluminide alloy subjected to creep at 760C and 276 MPa. Aged creep curve exhibits interfacial $\beta_{0,sec}$ precipitates [50].

through the lath structure resulting in Orowan strengthening. Creep response typical of a titanium aluminide alloy containing interfacial beta phase precipitates results in a faster reduction in strain rate, a lower minimum strain rate, and a prolonged tertiary creep stage resulting in extended rupture times (Figure 2.17).

Additionally, when a metastable fully lamellar microstructure is subjected to creep stress at elevated temperature, the dynamic precipitation of interfacial precipitates may occur due to the elevated temperature condition acting as a thermomechanical heat treatment [52]. In this scenario, the dynamic precipitation of interfacial precipitates may influence the strengthening behaviour in a different manner than that of the aged alloy. It has been found that the dynamic precipitation that occurs during creep at a lower temperature compared with the stabilization heat treatment results in both a finer precipitate size and greater volume fraction. The result of dynamic interfacial precipitation during creep is a reduction in the steady-state strain rate to a value comparable to the aged alloy. Thus the selection of starting microstructure will play a significant role in dictating the tradeoff between minimum creep rate / primary creep and rupture life depending on the in-service application (i.e. temperature, stress, and allowable strain).

Group B un-modified TNM alloys have been subjected to constant load creep studies at low stress [28]. As expected, fully lamellar microstructures result in the

greatest creep resistance, however a tradeoff exists in terms of tensile strength and elongation. For example, the TNM alloy taken through a two-step heat treatment plus a stabilization heat treatment results in the highest volume fraction of lamellar colonies, however the elongation at RT is on the order of 0.8 %. Elongation may be improved through a cyclic heat treatment process but a drop in both yield strength and creep strength occurs to a value close to that of the original cast/HIP starting microstructure. Additionally, when the β_0 phase decomposes to ω_0 , the influence on creep response has yet to be reported in the literature.

2.3.2 Ductility Improvements

Recent studies [26] performed on a Ti-45Al-x(Nb,Mo)-0.2B (at.%) beta solidifying TiAl indicate that the Nb and Mo β stabilizing additions have a significant effect on room temperature ductility and plasticity at elevated temperature. Nb/Mo additions on the order of 6 at.% produced a room temperature elongation of 0.8%. The same alloy with 2.6 at.% Nb/Mo additions achieved a room temperature elongation of 2.7% while maintaining the attractive fully lamellar microstructure [26]. Evaluating the plasticity of these alloys reveals that superplastic elongation (200-310%) is obtained at temperatures between 1050-1100 °C. Plasticity remains relatively high (50% at 1050 °C) with increasing strain rate, indicating the potential for near conventional rolling or stamping below the eutectoid transformation temperature [47].

2.4 Processing Routes

Various processing routes may be employed to produce TiAl. Ingot casting, investment casting, and P/M are the primary routes with follow-on processing methods such as hot working, extrusion, machining, and joining methods to produce near net shape components as shown in Figure 2.18. Casting is advantageous since it utilizes mature technology to produce billets of significant size that may be further processed into standard shapes such as sheet and rod through extrusion and hot rolling methods. However, the drawback to ingot casting for TiAl alloys is the lack of chemical homogeneity that results from density differences in the melt, and the potential peritectic solidification path during relatively slow cooling [56]. Macrosegregation of aluminum on the order of ± 2 at.% may lead to difficulties in controlling the processing of these alloys to achieve consistent mechanical properties through hot forging or extruding

Figure 2.18: Select process routes for TiAl (Adapted from [40, 57]).

methods [57]. Additionally, other casting defects such as porosity and shrinkage may result in detrimental properties that may require significant HIP'ing times, temperatures, and pressures to homogenize.

P/M routes for TiAl alloys involve the production of pre-alloyed powders through a rapid solidification gas atomization technique, followed by compaction of the powders by HIP'ing. P/M is advantageous for TiAl as it may achieve near-net complex shapes that reduce scrap, and further reduce the requirement for secondary operations such as hot working and machining [58]. P/M routes also eliminate casting defects, and are capable of producing a fine grained microstructure with relatively homogeneous distribution of phases and alloying elements. Defects associated with P/M of TiAl include the generation of coarse lamellae particles, the appearance of ceramic inclusions, and the appearance of microporosity [57, 58].

2.4.1 Hot Isostatic Pressing

HIP conditions along with particle size, morphology and composition affect both the level of consolidation, and microstructure of the HIP'ed alloy. For TiAl powders, temperatures and pressures in the range of 1000 °C and 100 MPa are required to produce full densification [59]. The phase fields associated with different HIP temperatures of beta gamma TiAl can be partially ascertained with assistance from the phase diagram shown in Figure 2.6. HIP'ing near the α transus temperature around 1300 °C for group B alloys promotes the formation of the α_2 phase at the expense of β and γ phases. HIP'ing near 1200 °C promotes the three phase $\alpha + \beta + \gamma$ microstructure [41]. Grain size will increase with increasing HIP temperature, and decrease with increasing HIP pressure. The higher HIP pressure provides more uniform dynamic recrystallization. Grain size uniformity of HIP'd samples may be improved through the use of a two step HIP procedure. The two step HIP procedure begins with a high temperature hold to homogenize the structure followed by a reduction in temperature to promote β phase formation. The benefit of such a temperature profile when compared with a single HIP holding time and temperature yields a more evenly distributed grain size [40]. For beta gamma TiAl alloys, the HIP procedure results in a near-gamma three phase ($\alpha_2 + \gamma + \beta$) microstructure as shown in Figure 2.7d with an average grain size between 2-4 μm and a β phase volume fraction of approximately 10% [40]. The two step HIP procedure applied to the group B beta gamma TiAl results in a relatively high volume fraction of β phase which may be beneficial for wrought processing [13]. Also, the fine grain size and relatively even distribution of the β phase throughout the matrix is advantageous due to a reduction in flow localization during forging or extrusion [13]. The as-HIP'd beta gamma TiAl microstructure exhibits potentially attractive features for hot working and machining.

2.5 Joining Titanium Aluminides

2.5.1 Conventional Brazing

Brazing is a liquid-phase solidification technique whereby a filler interlayer is raised above its melting point and drawn by capillary action into a gap between two substrate materials to be joined. The two substrate materials have melting points greater

Figure 2.19: Two step HIP temperature profile applied to beta gamma TiAl

than the filler interlayer. A chemical bond is formed between the filler interlayer and substrate material once proper wetting, spreading, and solidification of the filler interlayer occurs through controlled cooling. Bonding can be metallic, ionic, covalent or a mix of ionic-covalent depending on the composition of the substrate and filler interlayer involved [60]. An advantage associated with conventional brazing is the ability to minimize substrate microstructural changes due to the limited holding time at the brazing temperature. In conventional brazing, dwell times at the brazing temperature are short, and heating may be localized to the joint area so that long range diffusion is suppressed, allowing the substrate material to maintain its microstructural integrity. However, a significant drawback of conventional brazing is the limited high temperature serviceability and stability of the resulting joint [60]. The significantly lower melting point of the resultant braze zone may limit the ability to place hot-section repaired components back in service. In addition, the strength of the braze zone at high temperature may not approach that of the substrate material.

The thermal cycle associated with conventional brazing is similar to that of a solid-state heat treatment process. The substrate material to be joined along with the filler interlayer are subjected to three process steps. First, all components are heated ensuring the homogeneous warming of the components to avoid unwanted thermal stresses, which may lead to cracking of the substrate material. During this stage, dwell steps may be incorporated if parts are sufficiently large or if a reducing

atmosphere requires a minimum vacuum level to avoid oxidation of the substrate material faying surfaces. The assembly is raised to a temperature above the liquidus of the filler interlayer, but below the solidus of the substrate materials. Once complete wetting of the substrate material faying surfaces has occurred, the temperature is lowered at a controlled cooling rate causing solidification of the filler interlayer. Once solidification of the filler interlayer is complete, the parts are quenched or furnace cooled to room temperature, followed by post-bond heat treatments (PBHT) to homogenize the microstructure. The methods utilized for heating include induction, microwave, and vacuum furnace brazing technologies.

2.5.2 Diffusion Brazing / Transient Liquid Phase Bonding

Binary Eutectic System

In binary eutectic systems, the melting point of an alloy is a function of composition. If a low melting point, fast diffusing foreign solute filler metal is coupled with a substrate material capable of accepting the foreign diffusing solute, one may exploit the transient effects associated with composition change under steady-state isothermal conditions to facilitate the solidification of the filler metal. Specifically, during isothermal solidification the displacement of the solid/liquid interface that moves towards the centerline of the joint occurs due to the diffusion of the liquid filler into the solid substrate driven by the concentration gradient in the substrate [61]. The isothermal solidification process are governed by Fick's second law where for the case of unidirectional diffusion:

$$\frac{\partial C^\alpha}{\partial t} = D_s \frac{\partial^2 C^\alpha}{\partial y^2} \quad (2.1)$$

where C^α is the concentration of the foreign element in the solid substrate and D_s is the diffusion coefficient of the foreign element in the solid substrate. Under such conditions the concentration profile in the solid substrate follows a typical error function solution and the advancing solid/liquid interface tends to obey parabolic growth. However, departure from parabolic growth is possible as the effects of interface curvature and short circuit diffusion pathways such as the existence of grain boundaries tend to reduce the overall time to complete isothermal solidification.

The diffusion brazing / TLP bonding process (DB/TLP), in comparison to conventional brazing, necessitates a rapidly diffusing melting point depressant (MPD).

Diffusion of the MPD drives the solidification process by raising the remelt temperature at the advancing solid/liquid interface, as opposed to solidification through a cooling rate. As such the diffusivity of the MPD in the parent material must be sufficiently high to necessitate an acceptable flux into the substrate material in order to complete the isothermal solidification process within a reasonable timeframe.

A full schematic (Figure 2.20) reveals the mechanisms associated with the TLP process for a binary eutectic system. Five stages are associated with the TLP bonding process, and are listed as follows:

1. Stage 1: Interdiffusion during heating (Figure 2.20a)
2. Stage 2: Dissolution of the filler material (Figure 2.20b)
3. Stage 3: Homogenization of the liquid layer (Figure 2.20c)
4. Stage 4: Isothermal solidification (Figure 2.20d)
5. Stage 5: Homogenization of the joint microstructure (Figure 2.20e-f)

Stage 1 consists of heating the brazement from room temperature to the melting point of the filler metal. Interdiffusion may occur between the filler and parent material as solute atoms diffuse from the filler to the parent material and vice versa. Ramp time and filler gap width play an important role in the ability of solute to diffuse out of the filler alloy. Only in situations where the heating rate is very slow, or the filler interlayer is less than $2\text{ }\mu\text{m}$ will significant interdiffusion take place during this stage [62]. Stage 2 involves the dissolution of the filler material. During heating from the melting point to the isothermal holding temperature, solute atoms will diffuse from the filler into the parent material with a mutual diffusion of substrate atoms into the liquid. When the solubility limit in the parent material is reached, the parent material will dissolve into the liquid, and growth of the liquid zone width occurs (Figure 2.20b). Once the brazing temperature is reached, the liquid will be supersaturated with solute atoms. At the brazing temperature, diffusion of solute atoms in the liquid occurs until the concentration profile in the liquid flattens to the solubility limit. To achieve this state, the liquid layer will widen until a maximum width is reached (Stage 3 - Figure 2.20c), which typically takes only seconds to complete due to rapid diffusion in the liquid. Following homogenization of the liquid layer, isothermal solidification (Stage 4 - Figure 2.20d) takes place by holding

Figure 2.20: Schematic Illustration of the TLP bonding process applied to a binary eutectic alloy [61].

at the brazing temperature for an extended period of time. Solute atoms will diffuse from the liquid filler back to the parent material causing the liquid layer to narrow producing a solid with a composition of $C^{L\alpha}$. Assuming similar parent materials, the solid/liquid interface fronts will move towards each other until they meet at the middle of the joint completing isothermal solidification (Figure 2.20e). Since this process is controlled primarily by the width of the liquid layer, and the relatively low solid state diffusion of the solute into the parent material, holding times are typically on the order of hours. Following isothermal solidification, a concentration gradient will typically exist from the center of the joint to the substrate. Further homogenization of the joint (Stage 5 - Figure 2.20f) through heat treatments are conducted to further diffuse the solute into the parent material, reducing the concentration gradient at the centerline of the joint to produce a more homogeneous concentration gradient.

A comprehensive analytical description of the TLP process has been presented for binary eutectic systems, and the parameters that control the kinetics of isothermal solidification in these systems are well understood [61]. Typically, there exists an optimum brazing temperature at which time for completion of isothermal solidification is shortest. By increasing the brazing temperature above this optimum, the solubility of the MPD in the parent material may decrease such that the overall MPD flux into the parent material decreases despite an increase in the diffusion rate [61]. A single phase moving boundary model is typically employed to compute:

1. The composition across the joint.
2. The advancing solid/liquid interface and maximum liquid layer.
3. Time to complete isothermal solidification.

The assumptions typically associated with such analytical models include:

1. The densities of the solid and liquid phase are equal and constant.
2. The diffusion coefficient of each solute is only dependent on temperature.
3. Local equilibrium exists at the solid/liquid interface.
4. The solid/liquid interface remains planar.
5. Diffusion occurs perpendicular to the solid/liquid interface (1-D).

Using a two-phase analytical approach, an expression for the time for complete isothermal solidification was derived by Lesoult (cited in [63]). A mass balance approach was utilized presuming the moving solid/liquid interface was proportion to the root of time such that:

$$X(t) = k\sqrt{4Dt} \quad (2.2)$$

where k is a rate constant. An expression for the rate constant was solved using an error function of the form:

$$\frac{C_{\alpha L} - C_O}{C_{L\alpha} - C_{\alpha L}} = \sqrt{\pi} \frac{k(1 + \operatorname{erf}(k))}{\exp(-k^2)} \quad (2.3)$$

Figure 2.21: Concentration profile of a diffusing element across a half joint seam during isothermal solidification of TLP bonding [65].

where $C_{\alpha L}$ is the solute concentration at the interface, and C_O is the initial concentration of the MPD solute in the parent metal. Knowing the rate constant, the time to complete isothermal solidification is determined from equation 2.2 above as:

$$t = \frac{W_{max}^2}{16k^2D} \quad (2.4)$$

where W_{max} is the maximum width of the liquated region obtained during dissolution by:

$$W_{max} = \frac{C_F W_O}{C_{L\alpha}} \quad (2.5)$$

where C_F is the original solute concentration in the filler, W_O is the original filler width, and $C_{L\alpha}$ is the solute concentration at the surface.

The analytical solutions to these models involving the error function (equation 2.3) assume infinite or semi-infinite length scales, or gaussian solutions that assume a thin uniform filler material [64]. The finite thickness of the filler and parent material make an accurate analytical solution to the TLP process difficult [65]. Numerical solutions that account for the non-uniform composition distribution in the liquid and solid as well as addressing the moving solid/liquid boundary layer have resulted in greater success in predicting microstructure evolution during the TLP bonding

process [64, 66].

Multi-Component Systems and Intermetallic Formation

The role of additional alloying elements such as those in complex multi-component systems will affect TLP bonding mechanisms. In the binary case, during isothermal solidification the equilibrium tie-line that dictates the composition of the growing solid at the solid/liquid interface is fixed based on the solidus and liquidus isotherms associated with the MPD at the bonding temperature. However, for a solid solution metallic system composed of three elements, the equilibrium tie-line associated with the growing solid at the solid/liquid interface position may shift during isothermal solidification [67–69](Figure 2.22a). When a second solute is present with a significant diffusivity contrast or solubility contrast compared with the first solute, the solid/liquid equilibrium tie line shifts to maintain the coupled mass balance. As a result, two parabolic kinetic regimes are associated with the solid/liquid interface movement instead of a single kinetic regime associated with a single MPD. As a result, the interface movement is generally retarded at longer isothermal solidification times once the faster diffusing species has completely diffused into the parent material, and the slower of the two MPD's becomes the dominant diffusing species (Figure 2.22b).

Further to the ternary solid solution case, a review of the TLP process has been conducted by Schnell [62] who found the following main characteristics associated with multi-component systems:

1. The kinetics of the solid/liquid interface are controlled by the fastest diffusing element.
2. The liquid concentration and solubilities of the solutes in the solid constantly change due to interdiffusion of all elements during the TLP process.
3. The solute MPD concentration in the solid at the solid/liquid interface does not equal the MPD solubility in the solid during in-situ phase formation.
4. MPD precipitates that form in the parent material may have solvus temperatures higher than the brazing temperature resulting in a stable MPD precipitate phase.

Figure 2.22: (a) Shift in tie-line during isothermal solidification of a ternary solid solution system resulting in a continuously varying solid and liquid composition during isothermal solidification, (b) Resultant two kinetic regimes associated with the isothermal solidification tie-line shift in the Al-Zn-Sn system. [68]

5. The formation of MPD precipitates will influence the TLP process kinetics.

The above binary and ternary models are limited to solid solution systems and do not take into account a number of other factors that influence the interface kinetics during DB/TLP bonding. Additional factors that affect the kinetics of the DB/TLP process include but are not limited to:

1. Grain boundary grooving as a result of enhanced grain boundary diffusion.
2. Extrusion of the liquid from the joint.
3. Evaporation of the liquid from the joint.
4. Interface curvature effects due to the morphology of the solid/liquid interface.
5. Intermediate phase formation at the solid/liquid interface, or at solid/solid interfaces.

To take into account the additional factors that affect the kinetics of the advancing solid/liquid interface, MacDonald and Eagar defined in general terms the solid/liquid interfacial rate based on a number of fluxes such that [70]:

$$\frac{\partial W}{\partial t} = \frac{\rho_l}{\rho_s}(J_D + J_I) + J_V + J_X \quad (2.6)$$

where W is the width of the interlayer, ρ_l and ρ_s are the density of the liquid and solid phases respectively, and the subscripts of the fluxes refer to diffusion in the solid (J_D), intermetallic formation (J_I), evaporation of the MPD (J_V), and extrusion of the interlayer liquid from the joint (J_X).

When the substrate/filler composition associated with the metallic system contain intermediate phases or intermetallic compounds (IMC's), the kinetics of the DB/TLP process may differ from that of a typical solid solution DB/TLP process. For example, MacDonald and Eagar found that for systems driven by a combination of IMC formation and bulk diffusion in the substrate, the time for complete isothermal solidification was reduced an order of magnitude in time (i.e. from hours to minutes) at typical bonding temperatures [70]. Such IMC formation likely occurs during at least one of two scenarios:

1. Dissolution of substrate atoms into the liquid until saturation of the liquid results in heterogeneous nucleation of an IMC at the solid/liquid interface to achieve equilibrium at the solid/liquid interface.
2. In-situ IMC formation at solid/solid interfaces due to a metastable equilibrium condition between solid phases within a growing isothermally solidified joint.

For the first scenario, IMC nucleation and growth occurs at the solid/liquid interface when metastable equilibrium is achieved between the parent material and the liquid filler due to the thermodynamics associated with the metallic system during the early stages of diffusion brazing at the isothermal hold temperature. A typical example of such a system is the Cu-Sn system utilized for lead-free soldering, where a number of intermediate phases or compounds exist between the liquid Sn solder and the solid Cu substrate under typical bonding temperatures (Figure 2.23). Free energy profiles within the Cu-Sn system at 523K reveal that the liquid Sn and Cu substrate co-exist under metastable conditions at the bonding temperature. (Figure 2.24). Thus, heterogeneous nucleation and growth of an IMC phase will occur driven by the lower gibbs free energy (ΔG_v) associated with one of the intermediate phases compared with that of the α/L interface. The nucleation of the first intermediate phase to form may be determined by nucleation theory, where the heterogeneous nucleation barrier is defined by:

Figure 2.23: Cu-Sn binary phase diagram indicating the η and ϵ intermediate phases at 523K [71].

$$J = J_0 \exp \left[-\frac{16\pi\sigma_{sl}^3}{3kT(\Delta G_v)^2} \left(\frac{\cos^3\theta - 3\cos\theta + 2}{4} \right) \right] \quad (2.7)$$

where the driving force for nucleation is dictated by the surface energy and the difference in gibbs free energy. Tangent line construction is utilized in binary systems to determine the gibbs free energy difference for the various metastable conditions, while a tangent plane construction may be utilized in the ternary case.

Under the Cu-Sn scenario at 523K, the driving force for nucleation is greater for the η phase as opposed to the ϵ phase, therefore the η phase will precipitate and grow at the existing solid/liquid interface. However, once the η phase has formed a continuous layer between the solid and the liquid, a new metastable condition exists between the Cu substrate and the η phase, leading to the potential for in-situ (scenario 2) ϵ phase nucleation and growth due to the same heterogeneous nucleation mechanism. In-situ phase formation in ternary systems has also been observed in nickel based superalloy TLP joints [62].

Figure 2.24: Gibbs free energy profiles of various phases in the Cu-Sn system at 523K. Tangent line construction dictates that the solid/liquid interface is metastable, and that the η phase is the likeliest phase to precipitate at the solid/liquid interface due to the lower ΔG_v associated with this phase compared with the solid (α) phase or ϵ phase. [72]

When a third element is introduced into such a system, the kinetics of the intermediate phase growth may be significantly altered. For instance, when dissolution of nickel occurs into the growing intermetallic compound at the solid/liquid interface in the Cu-Sn-Ni system, the driving forces change such that the diffusion fluxes of all three components (Cu, Sn, and Ni) increase within the $(\text{Cu,Ni})_6\text{Sn}_5$ layer but the diffusion flux of the Sn and Cu components subsequently decrease in the $(\text{Cu,Ni})_3\text{Sn}$ layer [73]. Therefore the $(\text{Cu,Ni})_6\text{Sn}_5$ layer will dominate the layer growth and the Cu_3Sn layer will be suppressed and potentially disappear, causing a change in the kinetics of the advancing solid/liquid interface. If constituents other than the MPD form the IMC's, an increase in bonding time will result as the MPD must now diffuse through the IMC phase which generally has lower diffusivity than a solid solution substrate material [74].

Liu et al. [75] formulated a model that considers the formation of an intermetallic reaction product between an intermetallic compound and a solid-solution phase. In this model, the time to grow the intermetallic reaction product was assumed to follow parabolic time dependent growth such that:

$$\ln t_0 = \ln \left(\frac{Z^2}{2K_0} \right) - \frac{Q}{RT} \quad (2.8)$$

where Z is the thickness of the intermetallic layer, K_0 is the pre-exponential factor, and Q is the activation energy. Growth of the IMC generally follows parabolic growth law indicating that the growth rate is diffusion controlled. However different morphologies lead to different exponentials associated with the typical parabolic relationship. Planar growth is typified by a power law exponent of $n=2$, while a cellular/scalloped morphology is typified by a power law relationship of $n=3$ [76]. Thus the growth rate of the advancing solid/liquid interface is influenced not only by the diffusing species but also by the morphology of the advancing solid/liquid or solid/solid interface.

2.5.3 Braze Filler Alloys

When determining a suitable filler alloy for TLP bonding, the following characteristics are generally required;

1. A simple binary alloy to keep the joint design as simple as possible.
2. A phase constitution with a low melting point eutectic or peritectic reaction.
3. Minimize the formation of brittle intermetallics that may create diffusion barriers leading to brittle interlayers.
4. The terminal primary phase should possess a wide range of solubility of the other alloying elements. Greater solubility mitigates the risk of precipitating intermetallic phases on cooling and provides greater tolerance on the amount of filler material introduced into the joint area.

Titanium aluminides form oxides at elevated temperatures. The high melting point of these oxides prevents wetting of the substrate during the brazing process when conducted in air. Therefore, high temperature brazing of TiAl is typically conducted under a vacuum or inert atmosphere to suppress the formation of oxides and allow proper wetting of the substrates. The inert atmosphere is typically dry argon, and reduces potential oxidation contamination of the adjoining surfaces that may lead to a poor joint containing unwanted porosity. Without PBHT, conventional TiAl brazed joints typically exhibit an inhomogeneous microstructure containing significant amounts of intermetallic phases. For TiAl alloys, braze filler compositions

that exhibit good wettability, adequate brazing temperature, and retain their mechanical and chemical properties have been difficult to realize [57]. Base compositions attempted in the research community [57] include the following broad classes with detailed compositions listed in Table 2.2 :

1. Ni and Co-based braze alloy containing C, B, or Si additions
2. Precious metal braze alloys such as Ag, and Pd
3. Ti based braze alloys containing Cu, Ni, and Zr

Ni and Co based braze alloys containing B, Si, and C additions aid in reducing the melting temperature but result in the formation of brittle precipitates. Precious metal braze alloys have poor wettability and significantly erode the base materials [57]. Ti-based braze alloys have shown the greatest promise in terms of mechanical properties and quality of the resulting joint with melting point depressants (MPD) such as copper and nickel. Filler metals including Ti-15Cu-15Ni and Ti-Zr-Cu-Ni are suitable for brazing titanium aluminides. Joint strengths resulting from these filler alloys are on the order of 40-50% of the base metal's (yield) strength [77]. In the case of the Ti-Cu-Ni system, the nominal composition of a typical braze alloy is 70Ti-15Cu-15Ni (wt.%). The maximum solubility of Cu and Ni in a typical γ -TiAl alloy is approximately 2% for Cu at room temperature and 0.6 % for Ni at 900 °C [78, 79]. Therefore, given the composition of the filler alloy, potential intermetallic compound formation is anticipated within the brazed joint.

Brazing trials in Table 2.2 were typically performed under a vacuum environment ranging from 10^{-3} to 10^{-4} torr, or in an inert atmosphere. Filler materials were produced in foil form ranging in thickness from 50 μm to 200 μm [77, 82–89]. Additionally, the utilization of powder+binders for the filler materials was attempted by [80, 82]. Processing times and temperatures varied widely given the multitude of interface geometries and compositions attempted. Based on Table 2.2, brazing temperatures range from 880-1200 °C with holding times ranging from 30 seconds to 30 minutes.

Titanium Aluminide Braze Joint Evolution & Microstructure

For conventional brazing of γ -TiAl, nickel based filler alloys typically exhibit intermetallic compounds at the joint interface. The microstructure of the brazed joint,

Table 2.2: Base and filler compositions for joining TiAl materials through conventional brazing

Parent Mat'l	Filler	Filler Type	Thk. (μm)	Braze Type	Ref.
Ti-43Al-9V-0.3Y	TiH ₂ -50Ni	Powder	NR	Furnace	[80]
γ -TiAl 47XD	VPr-16*	NR	NR	Furnace	[81]
γ -TiAl 47XD	VPr-28*	NR	NR	Furnace	[81]
Ti-48Al	Ti-37.5Zr-15Cu-10Ni	Tape	200	Furnace	[77]
Ti-48Al	Ni-27Ti-10Al	Tape	200	Furnace	[77]
Ti-46Al-4(Cr,Nb,B)	Ti-15Cu-15Ni	Foil	100	Furnace	[82]
Ti-46Al-4(Cr,Nb,B)	Ti-15Cu-15Ni	Powder	0	Furnace	[82]
Ti-50Al	Ag	Foil	100	Infrared	[83]
Ti-47Al-2Cr-2Nb	Tini67*	Foil	50	Furnace	[84]
γ -Met100*	Ag-21Cu-15Pd	NR	NR	Furnace	[85]
γ -Met100*	Au-30Ni	NR	NR	Furnace	[85]
γ -Met100*	Pd-40Ni	NR	NR	Furnace	[85]
γ -Met100*	metglass*	Foil	NR	Furnace	[85]
γ -Met100*	Ti-15Cu-15Ni	NR	NR	Furnace	[85]
γ -Met100*	Ti-33Ni	NR	NR	Furnace	[85]
Ti-47Al-2Cr-2Nb	Ticuni*	Foil	90	Furnace	[86]
Ti-50Al	Al	Foil	75	Infrared	[87]
Ti-50Al	BAlSi-4*	Foil	75	Infrared	[87]
Ti-50Al	BAg-8*	Foil	100	Infrared	[88]
Ti-47Al-4.8Nb-2.7Cr	Al-Si	Foil	70	Infrared	[89]

Note: The composition for γ -Met100 is Ti-46.5Al-4(Cr,Nb,Ta,B), VPr-16 is Ti-24Zr-13Zr-9Ni, VPr-28 is Ti-33Zr-16Cu-15Ni, Tini67 is Ti-33Ni, metglass is unknown, Ticuni is Ti-15Cu-15Ni, BAlSi-4 is Al-(11-13)Si-0.3Cu-0.1Mg-0.2Zn-0.15Mn-0.8Fe, BAg-8 is Cu-(71-73)Ag .

Figure 2.25: SEM micrograph of a TiAl alloy vacuum brazed for 15 min at 1180 °C using a TiH₂-50 wt % Ni powder filler alloy. [80]

shown in Figure 2.25, exhibited an interfacial zone on the order of 100 μm comprised of a diffusion layer with a Ti₃Al phase (grey), a brazed zone (white) composed of Al₃Ti+Ni₄Ti₃, and a Ti₃Al (grey) phase distributed within the brazed zone intermetallic structure [80]. With increased brazing temperature, the volume fraction of these intermetallics in the braze zone was reduced and replaced by TiAl. It was found that at brazing temperatures lower than 1140 °C incomplete bonding occurred, while brazing temperatures above 1200 °C produced significant erosion of the base material. Nickel based braze filler alloys were also attempted by Shapiro et al. [77], however wetting of the TiAl substrate did not occur in the 1180-1200 °C temperature range. It was postulated that oxide formation occurred on the TiAl substrate surface before the braze liquidus temperature was reached (1120 °C), resulting in an incomplete bond under a vacuum of 10⁻⁴ torr. Tabernig et al. [85] found nickel based braze alloys attractive for their oxidation resistance. However, at high temperatures, these braze alloys formed undesirable borides and silicides exhibiting extreme brittleness.

Multicomponent titanium based braze alloys containing zirconium as an MPD typically exhibit a eutectic phase in the joint area when bonding γ -TiAl. The commercial VPr braze alloys produces a eutectic structure as shown in Figure 2.26 [81]. Strength tests performed on these joints typically exhibited premature failure in the eutectic region. Shapiro et al. [77] also conducted brazing trials on hot pressed and annealed γ -TiAl (Ti-48Al (at%)) alloy, with the filler metals in the form of pre-alloyed

Figure 2.26: Microstructure of a brazed joint between γ -TiAl and VPr-16 filler alloy (x1000) [81].

powders suspended in a 0.008 inch thick transfer tape. Ti-based powder braze materials with zirconium additions brazed at 1180 °C also produced a eutectic zone. Brazing the same filler alloys at lower temperatures in the range of 880-900 °C resulted in a combination of eutectic and brittle $(\text{TiZr})_2\text{Cu}$ intermetallic phases in the braze zone [77]. Shear test results show an improvement in the intermetallic free joint compared with the joint produced at the lower brazing temperature. The corresponding joint shear strength utilizing the Ti-37.5Zr-15Cu-10Ni filler alloy was 355 MPa at room temperature, increasing to 452 MPa at 650 °C, followed by a drop at 800 °C to 307 MPa [77].

Titanium based braze alloys with copper and nickel additions have been extensively researched as potential braze filler alloys. Wallis et al. [82] found that a Ti-15Cu-15Ni (wt.%) braze alloy is relatively forgiving of process parameters and produces similar joint strength regardless of the processing conditions. Microstructures at the joint in Figure 2.27 show a complex transition from the two phase ($\gamma + \alpha_2$) region to a largely continuous α_2 structure (points A1, B1, and C1) followed by a fine grained multi-phase region near the center of the joint (points E1, F1, and G1). Based on EDS analysis and review of the ternary phase diagram for Ti-Al-Ni(Cu), Wallis postulated that a τ_3 reaction phase formed on cooling which transformed to a stable τ_4 phase with prolonged aging at 700-800 °C in the central portion of the joint as shown in Figure 2.28. The microstructure varied with brazing time (10-30 min) and braze filler thickness (0-30 μm). However, shear strength remained relatively

Figure 2.27: Microstructure of Ti-Cu-Ni brazed joint at 1040 °C for 10 minutes [82].

Figure 2.28: Microstructure of the Ti-Cu-Ni brazed joint at 1000 °C for 30 minutes followed by exposure to 700 °C for 1000 hours [82].

consistent with aging, gap thickness, and applied pressure.

The evolution of joint microstructure during infrared brazing of binary titanium aluminide with a Ti-15Ni-15Cu (wt.%) braze alloy was studied by Lee et al [90]. The evolution of the joint microstructure was found to involve a number of steps (Figure 2.29). It was found that aluminum atoms from the substrate primarily dictated the evolution of the microstructure at short isothermal solidification times on the order of 30-60 seconds. Initially, Al dissolution from the solid/liquid interface resulted in the formation of a continuous β phase layer and associated $L + \beta$ mushy zone (Figure 2.29a). With longer holding times the metastable β/γ interface results in the nucleation and growth of a columnar α phase within the β phase resulting in a two phase $\alpha + \beta$ region emanating from the substrate interface (Figure 2.29b). With extended holding times, the two phase $\alpha + \beta$ phase region continues to evolve until three distinct regions of single phase β , α_2 , and α phase with high Al content eventually emerge (Figure 2.29e). The results of Lee et al. reveal the complex and sensitive microstructural evolution that depends on a number of factors including the base metal composition, base metal microstructure, braze filler MPD, bonding temperature, holding time, and cooling rate.

Brazing experiments performed by Guedes et al. [86] utilizing a commercial Ti-Cu-Ni braze filler at 980-1000 °C for 10 minutes, produced three distinct reaction layers composed of $\alpha_2 + \text{Ti}(\text{Ni,Cu})\text{Al}$ (layer A), α_2 (layer B), and $\alpha_2 + \text{Ti}_2(\text{Ni,Cu}) + \text{Ti}(\text{Ni,Cu})_2\text{Al}$ (layer C), where layer A was near the substrate, and layer C was the central portion of the joint, as shown in Figure 2.30. Hardness values of all the reaction layers were found to be higher than the parent material ($\alpha_2 + \gamma$) matrix, and the width of the joint area slightly increased with an increase in brazing temperature. No further homogenization of the joint was attempted.

Guedes et al. [84] also conducted brazing experiments utilizing a Ti-Ni braze alloy (Tini67). Microstructure in the brazed joint conducted at 1000 to 1200 °C produce two distinct reaction layers, one composed of α_2 near the substrate (layer A), and the other composed of TiNiAl intermetallics near the center of the joint (layer B) as shown in Figure 2.31a. Between 1150-1200 °C an additional γ phase was detected in the reaction layer A indicated by the arrows as shown in Figure 2.31b. It was postulated that the dissolution and diffusion of γ -TiAl played a significant role in the formation of the microstructure. Additionally, Ti-33Ni (wt.%) brazing experiments

Figure 2.29: Schematic microstructural evolution of a binary TiAl alloy subjected to infrared brazing with a Ti-15Ni-15Cu (wt.%) braze alloy at 1150 °C. [91].

Figure 2.30: Microstructure of the Ti-Cu-Ni brazed joint at 980 °C for 10 minutes [86].

conducted by Tabernig et al. [85] reveal Ni-rich Ti_2AlNi plus α_2 in the center of the joint. Ultimate tensile strength (UTS) at room temperature was 440 MPa and 380 MPa at 700 °C, approaching 80% of the base material strength.

Pure Ag as a filler braze has been attempted by Shiue et al. [83]. Shiue found that brazing in the 1050-1100 °C range for one minute produces a three phase microstructure in the joint area consisting of $\text{Ti}(\text{Al},\text{Ag})$ (dark) phase, $\text{Ti}_3(\text{Al},\text{Ag})$ (grey) phase, and an Ag-rich (white) phase, as shown in Figure 2.32. The formation of the Ti_3Al phase was a consequence of dissolution of the TiAl substrate. Shear strength was reported to exceed 385 MPa with failure located at the TiAl substrate for lower brazing times and moving to the the Ag-rich braze matrix with increased brazing time above 60 seconds.

Shiue et al. [88] also investigated the use of a commercial BAg-8 filler alloy to join $\gamma\text{-TiAl}$. Brazing trials were conducted at 950 °C for 30-180 seconds. Microstructures reveal that Ag did not react with the substrate, but that copper reacted vigorously with TiAl. The copper is consumed by the TiAl resulting in a change in composition of the filler towards a hypoeutectic composition. The result is the formation of an AlCuTi reaction phase (light grey marked by B) at the interface with a Ti_3Al intermetallic phase (dark grey marked by A), and an Ag-rich hypoeutectic phase (white

Figure 2.31: Microstructure of the Ti-Ni brazed joint at (a) 1000 °C and (b) 1200 °C showing the additional γ phase detected in reaction layer A for the 1200 °C case. [84].

Figure 2.32: Microstructure of the TiAl/Ag/TiAl specimen brazed at 1050 °C for 60 seconds. [83].

Figure 2.33: SEM BEI microstructure of the TiAl/BAg-8/TiAl specimen brazed at 1150 °C for 45 seconds. [88].

marked by C) as shown in Figure 2.33. Significant growth of the AlCuTi phase occurred with increased brazing time and temperature. The presence of the Ti_3Al phase is due to the increased dissolution of Al over Ti for the Ag-rich liquid. Shear strength is maximized with a brazing condition of 950 °C and a 1 minute holding time. Increased brazing time grew the AlCuTi reaction layer causing deterioration of shear strength.

Tabernig et al. [85] performed brazing experiments with various precious metal filler alloys. The use of pure Au and Pd based filler alloys was discounted due to poor wettability, and extensive erosion of the parent material that produced significant pores and cracks in the joint. However, a ternary alloy composed of Ag-21Cu-15Pd (wt.%) exhibited excellent wetting of the substrate and a crack/pore free joint. The resultant microstructure consisted of a Pd-rich globular phase within a soft Ag-rich matrix with a reaction layer consisting of a brittle $TiCu_2$ intermetallic. The UTS of the joint was 330 MPa at room temperature with a significant reduction in strength at elevated temperature. The oxidation resistance at elevated temperature limits the use of these braze alloys to temperatures around 400 °C [85].

Aluminum based alloys have also been investigated as a potential braze filler material. Shiue et al. [87] conducted brazing experiments on pure Al, along with commercially available BAlSi-4. Results for brazing at 900 °C for 30 seconds for pure

Figure 2.34: The SEI of TiAl/Al/TiAl specimen brazed at 900 °C for 30 seconds [87].

Al filler material revealed the formation of excessive TiAl₃ intermetallics in the joint as shown in Figure 2.34. The strength of the joint could not be evaluated due to fracture during sample preparation. Additionally, post bond heat treatments could not homogenize the structure and further investigations were abandoned.

For BAlSi-4 braze alloy, brazing experiments were conducted from 800-900 °C with holding times ranging from 60-300 seconds. Resultant microstructures revealed the formation of Si-rich and Al-Fe-Si intermetallics in the joint. For short brazing cycles, the AlSi₃Ti₂ phase was observed. For longer thermal cycles, the Al₁₂Si₃Ti₅ phase (marked as B) formed and grew along with a thin layer of TiAl₂ (marked as G), an Si-rich phase (marked as E), and an Al-Fe-Si intermetallic phase (marked as F), shown in Figure 2.35. At low brazing times, shear fracture occurred at the interface between the parent material and the filler alloy. With increasing brazing times, fracture occurred in the reaction layer, and then moved into the braze zone. Maximum shear strength occurred with brazing temperature at 900 °C and 120-300 second holding times.

Titanium Aluminide DB/TLP Joint Microstructure

Substantial research has been conducted into TLP bonding of γ -TiAl. Table 2.3 lists parent compositions, filler compositions, filler thickness, and filler type explored in

Figure 2.35: The backscattered electron image (BEI) of TiAl/BAlSi-4/TiAl specimen brazed at 900 °C for 300 seconds [87].

the research community related to TLP bonding of TiAl alloys. TLP bonding of TiAl has typically utilized a braze filler alloy containing an MPD such as copper, nickel, iron, aluminum or silver [77,92–96]. The key microstructural requirement on high-stress joints is the avoidance of undesired reaction products at the center of the joint [97]. Depending on the MPD utilized in the filler alloy, brittle phases may form and may detrimentally affect the mechanical integrity of the joint. Low remelting temperatures associated with the resultant reaction products in the joint may also hinder the maximum service temperature of repaired component.

Titanium based filler materials considered by Guedes et al. [84,93,96] have focused mainly on Ti-Cu-Ni or Ti-Ni foil based alloys utilized in conventional brazing with a goal of investigating the influence of processing parameters on the mechanisms that control the amount of residual filler metal contained at the bond line. Samples were diffusion brazed in a vacuum at 8×10^{-5} mbar in an electrical furnace at 1000 and 1100 °C. At 1100 °C, no residual braze alloy zones were detected and the center of the bond line contained a mixture of α_2 -Ti₃Al with Ti-Ni-Ti or Ti₂Ni intermetallic compounds (Figure 2.36a). Samples brazed at 1000 °C contained a substantial amount of residual filler (Ti₂Ni and Ti (α) particles) as shown in Figure 2.36b. It was concluded that the diffusion of aluminum into the interfacial zone was the main factor

Table 2.3: Base material and filler composition combinations attempted for joining TiAl materials through TLP bonding

Parent Mat'l	Filler	Filler Type	Thk. (μm)	Ref.
Ti-45Al-5Nb-0.2B-0.2C	Ti-29Fe	Foil	300-350	[32]
Ti-45Al-5Nb-0.2B-0.2C	Ti-24Ni	Foil	300-350	[32]
Ti-45Al-5Nb-(W,B,Y)	TiNi-Nb	Foil	100	[98]
Ti-48Al-2Cr-2Nb	Ti-(9-16.5)Ni	Foil	110-210	[99]
Ti-42.5Al-9V-0.3Y	TiNi-V	Foil	200	[100]
Ti-47Al-2Cr-2Nb	TiNi67	Foil	50	[84, 93, 96]
γ -TiAl 47XD	Ti-Zr-Fe	NR	NR	[81]
γ -TiAl 47XD	Ti-Zr-Mn	NR	NR	[81]
Ti-42Al-2Cr	Ti-(Cu,Ni,Fe)	Foil	10-50	[101]
γ -met PX	Ti-48Al-2Cr-2Nb+(0-3)Cu	Powder	NR	[102, 103]
γ -met PX	γ -TiAl-0.1B+(0-3)Cu*	Powder	NR	[102, 104]
γ -met PX	TiCuNi-70	Foil	50	[102]
Ti-42Al-2Cr	Ti-Cu-Ni-Fe	Foil	10-50	[105]
Ti-48Al-2Nb-2Cr	Ti-48-2Nb-2Cr+(0-3)Cu	Foil	300-350	[78, 106]
Ti-48Al-2Nb-2Cr	Ti-48-2Nb-2Cr+Cu	Powder	350-500	[107–109]
Ti-48Al-2Nb-2Cr	Ti-50Al+Cu	Powder	350-500	[109]
Ti-45-2-2-XD*	Pure Al	Foil	NR	[110]
Ti-45-2-2-XD*	Cu-Ni	Foil	NR	[110]
Ti-45-2-2-XD*	Pure Ag	Foil	NR	[110]
Ti-45-2-2-XD*	Ti-15Cu-15Ni	Foil	25	[110]

Note: The detailed composition for γ -TiAl-0.1B+(0-3)Cu is Ti-46.5Al-2.5Cr-1Nb-0.5Ta-0.1B+(0-3)Cu, for Ti-45-2-2-XD is Ti-45Al-2Nb-2Mn+0.8TiB₂ XD

Figure 2.36: BEI of the interface, showing the reaction zone (RZ), part of the central zone (CZ) and the loci where the EDS analysis was performed: a) joining at 1000 °C; b) joining at 1100 °C [93].

controlling the microstructural evolution of the interface, and was especially significant at temperatures slightly above the liquidus of the braze alloy. By increasing the dwell time, eliminating the residual braze zone may be possible. PBHT conducted on the brazed joints at 1250 °C and 1350 °C with dwell times of 240 and 30 minutes respectively, altered the microstructure to a two phase ($\gamma + \alpha_2$) microstructure with minimal TiNiAl retained particles [96].

Duan et al. [101, 105] also focused on conventional brazing foils as a filler material for TLP bonding. Alternating non-symmetric foil layers of various compositions were evaluated. Results indicate that for Ti-Cu foils, the transient liquid phase first appears in the Cu foil followed by the Ti foil. For Ni and Fe foils, the transient liquid phase first appears in the adjacent Ti foil. The different diffusion kinetics associated with each unique MPD resulted in differing levels of dissolution of the parent material depending on the MPD and interlayer configuration employed. Intermetallics in all cases formed and inhibited the use of PBHT to homogenize the structure. It was postulated that the PBHT temperatures attempted were not high enough to significantly alter the reaction layers formed during the joining process and that further experimentation into PBHT optimization is required.

Khorunov et al. [81] experimented with Ti-Zr-Fe and Ti-Zr-Mn compositions in order to reduce the eutectic volume fraction associated with Ti-Zr-based filler alloys. The reduction in eutectic phase was achieved through ternary filler compositions, as shown in Figure 2.37, with an indistinguishable fully lamellar microstructure across

Figure 2.37: Microstructure of the joint area between γ -TiAl and (a) Ti-Zr-Fe filler alloy, and (b) Ti-Zr-Mn filler alloy (x1500) [81].

the joint area. An improvement of strength at room and elevated temperature was achieved. Details of the thermal cycle, and composition of the filler materials were not directly reported. However, room temperature strength was measured to be 600-690 MPa.

Ti-based filler materials employing more than one MPD solute have been investigated by Butts et al. [102] and Chaturvedi et al. [110]. Ti-Cu-Ni ternary compositions at or near Ti-15Cu-15Ni (wt.%) were employed. Butts did not report time and temperature profiles for the brazing cycle, but found that the width of the bond increased by over 100% when compared to the original foil width, denoting a large amount of substrate dissolution during bonding. Compositional analysis in the bond region indicated dilution of Ni and Cu down to approximately 2 at.%. However, microhardness measurements suggest that the resultant phase in the joint may be one large intermetallic. Four point bend tests produce a strength of approximately 50% of the base material, suggesting that TiCuNi-70 braze foil may not provide acceptable mechanical properties under high stress conditions. Chaturvedi et al. [110] employed Ti-Cu-Ni fillers along with Cu-Ni/Ti/Cu-Ni interlayers with melting points lower than 1125 °C to avoid the eutectoid reaction in the fully lamellar γ -TiAl microstructure. Results of a 25 μ m thick Ti-15Cu-15Ni foil brazed at 990 °C for 30 minutes resulted in the formation of the α_2 phase in the joint, along with the dispersion of unknown intermetallic particles. A heat treatment between 1000-1100 °C was required for an extended time (2 days to 1 week) in order to dissolve the intermetallic phase formed during diffusion

brazing. Higher heat treatments resulted in the melting of the unknown intermetallic creating unwanted voids. Following the elimination of the unknown intermetallic, a further heat treatment at 1310 °C for 30 minutes was required to remove the α_2 phase in the joint and produce a fully lamellar microstructure. However, achieving the fully lamellar structure required a relatively thin foil thickness between 5-10 μm .

Chaturvedi et al. [110] postulated that aluminum based filler alloys may be an attractive alternative for TiAl alloys having Al content below a typical γ -TiAl alloys (i.e below 45-48 at.%). Al and Ti atoms in excess of stoichiometric TiAl composition may occupy antisites without creating vacancies (i.e. Ti atoms can be readily accommodated on Al sites and vice versa) [110]. Therefore both Ti, Al, and any other element with a strong affinity for Ti or Al should be able to diffuse into TiAl readily. Pure Al brazing experiments indicated excellent wetting and reaction with TiAl substrates, but with the formation of TiAl_3 intermetallic in the joint. Transformation of the TiAl_3 to γ -TiAl was possible with long PBHT. Therefore, if mechanical properties associated with conventional γ -TiAl alloys in the 45-48at.% Al range are acceptable within the joint area, pure Al filler with a specific thickness may be an alternative for TiAl alloys with lower aluminum content. However, this type of bond will generate an increasing Al concentration gradient from the parent material to the the center of the brazed joint and may or may not be acceptable depending on Al concentration tolerance limits.

An alternate approach called wide gap TLP joining has been extensively studied by Zhou and Gale et al. [78,102–104,107–109]. The wide gap TLP bonding technique utilizes a composite interlayer consisting of an MPD layer, and a non-melting layer similar in composition to the parent material. The non-melting layer acts as a diffusion sink, reducing the amount of liquid phase required, thus decreasing the bond time and suppressing microstructural changes in the parent material. Conventional TLP studies conducted with pure Cu foil interlayers on the order of 50 μm show that intermetallics are difficult to suppress, and that bonding times are too long for commercial purposes, unless the foil thickness is reduced to 5 μm [108,109].

Resultant as-bonded wide gap TLP microstructures for γ -met PX with varying TiAl composite interlayers reveals an as-bonded microstructure with no copper rich intermetallics and only a few regions of completely dissolved γ -met powders (See

Figure 2.38: Optical micrograph of an as bonded GMPX joint employing a 50:1 gamma met to copper interlayer ratio. Region (a) is an area of completely dissolved gamma met powder with a lamellar structure, and (b) porous regions observed [102].

Figure 2.39: Optical micrograph of an as bonded GMPX joint employing a 50:1 gamma met to copper interlayer ratio with a PBHT of 1290 °C for 24 hours [102].

Figure 2.40: Optical micrograph of an as bonded GMPX joint employing a 50:1 gamma met to copper interlayer ratio with a two step heat treatment of 1290 °C for 24 hours followed by 3 hours at 1340 °C. Light region is due to residual copper [102]

Figure 2.38). Upon further PBHT below the α transus temperature, a duplex microstructure, as shown in Figure 2.39, is achievable. The duplex microstructure is evident in both the bulk material and in the bond line with a coarser grain size in the bond line as compared with the bulk material. A further two step heat treatment at 1290 °C for 24 hours, followed by 3 hours at 1340 °C allows Cu diffusion into the bulk substrate. This PBHT above the α transus temperature generates a fully lamellar microstructure with an average colony size of $250 \pm 90 \mu\text{m}$, as shown in Figure 2.40 [102]. Butts et al. suggested that the solubility of the MPD is dictated by the volume fraction of the α_2 phase present in the microstructure prior to bonding. Differing substrate materials exhibited significantly differing copper solubility limits with the same filler composition and thermal cycle. Epitaxial growth of the interlayer particles was postulated as the primary mechanism for the rapid microstructural development at the bond line during isothermal solidification [107]. However, non-epitaxial γ growth was also observed in experiments where the main growth front was non-planar [108].

TLP Mechanical Properties

The high operating temperatures and stresses placed on rotating and stationary gas turbine components require extremely demanding mechanical integrity and stability

of the joint microstructure. Vanes and blades are subject to time dependent aging reactions due to high operational temperatures [111]. Vane crack repair is a typical application of TLP bonding where alloyed powders containing an MPD are utilized to raise remelt temperature of the bond for high temperature service and to provide a void free repair through the powder route [111, 112]. It is essential for reliability purposes that the joint exhibits a homogeneous microstructure of comparable composition, grain size, lamellar spacing, beta precipitation size, distribution, and morphology to ensure an excellent balance of room temperature and high temperature mechanical properties. Four point bend tests, tensile testing, and microhardness measurements have been conducted to characterize the TLP joint performance compared to the bulk material. Bend strength for as-bonded joints approach 70% of the bulk strength with values of $1100 \text{ MPa} \pm 160 \text{ MPa}$ compared with a bulk value of $1510 \pm 80 \text{ MPa}$ for gamma met PX cycled under the same thermal treatment with powder interlayers composed of a 50:1 gamma met to copper interlayer ratio [102]. For the same joint subjected to PBHT treatments with a fully lamellar microstructure, the bend strength reduced to $790 \pm 70 \text{ MPa}$, and the bulk material's bend strength also reduced to the same level of $790 \pm 80 \text{ MPa}$. Room temperature tensile tests performed on the as-bonded joint exhibit a tensile strength of $560 \pm 30 \text{ MPa}$ as opposed to $630 \pm 60 \text{ MPa}$ for the bulk material cycled under the same thermal conditions. With the addition of PBHT, joined specimens exhibited a tensile strength of $570 \text{ MPa} \pm 30 \text{ MPa}$ while the bulk materials obtained a strength of $580 \pm 50 \text{ MPa}$. For Ti-48Al-2Cr-2Nb at.% (Ti-48-2-2) substrates, four point bend tests resulted in an average bend strength of 580 MPa for samples bonded for 10 minutes at 1150 °C, and 540 MPa for samples subjected to a PBHT of 1350 °C for 1 hour [107]. Bulk Ti-48-2-2 subjected to the same thermal treatments exhibited bend strengths of 644 MPa and 639 MPa respectively. Fractography of the bonded and bulk materials revealed no correlation to failure within the joint or the bulk substrate, and no difference in fracture surface was evident between bonded and bulk specimens.

2.6 Summary

$\beta - \gamma$ TiAl is a relatively new alloy. The literature reveals promise in improving the ductility of TiAl through increased β phase volume fraction at the expense of

high temperature strength. Hot working and machining trials have proven the potential ductility improvements. Additionally, the P/M route applied to $\beta - \gamma$ TiAl is an attractive process that reduces secondary processing steps and produces near net shape components. With novel heat treatments, $\beta - \gamma$ TiAl may produce final microstructures with reduced β phase only at the lamellar interfaces. Additionally, the P/M route may provide nearly fully dense, homogeneous microstructures, with minimal segregation, porosity, and texture.

The literature has also revealed that joining γ -TiAl is a sensitive process. TLPB and diffusion bonding have shown the greatest promise for retaining high temperature mechanical properties by ensuring the resulting microstructure in the joint area resembles the parent material as closely as possible. Eliminating deleterious intermetallics in the bond area allows homogenization to proceed at a greater rate. However, limited solid solubility of MPD's in TiAl, cause difficulties in the appropriate selection of filler compositions, joint geometry, and processing conditions.

For TiAl/TiNi-67/TiAl diffusion brazing couples of group B $\beta - \gamma$ TiAl alloy, it is unknown if local equilibrium is established slowly or quickly at the solid/liquid interface. No atomic transport data exists for the diffusion of Ti, Al, or Ni in liquid eutectic Ti-24Ni at.%. Additionally, the composition range of the β phase at the isothermal solidification temperature is quite broad, thus it may not be reasonable to assume that the intermetallic phases produced through the brazing cycle do not change their composition and hence mass transport properties over time. Additionally, the potential for isothermal solidification via the growth of a cellular β phase which is not typical for conventional γ -TiAl alloys may significantly impact the kinetics of the diffusion brazing process for group B $\beta - \gamma$ TiAl alloys compared with conventional γ -TiAl alloys under similar bonding conditions. The change in constitution and size of the semi-continuous α_2 reaction layer, the availability of short circuit diffusion pathways, the impact of coarsening and precipitation within the diffusion zone, and the impact of substrate microstructural changes are key issues to understand the joining of group B $\beta - \gamma$ titanium aluminide intermetallics when utilizing the diffusion brazing process. In addition to the sensitivity of the diffusion brazing process as applied to microstructural evolution, the resultant creep performance of diffusion brazed group B P/M beta gamma alloys has not been reported in the literature and is critical to the successful joining and/or repair of hot section gas turbine components. Through the evaluation of an analytical power law growth model

associated with the TLPB joining process, an improvement in the ability to better understand the growth mechanisms associated with the joint microstructures will be realized. An understanding of the kinetics that drive specific microstructural changes, and how these changes affect the resulting mechanical properties of both the parent alloy and of brazed joints will help reduce trial and error methodologies for future experimental TiAl alloys. Additionally Group B $\beta - \gamma$ TiAl alloys show promise for primary creep performance due to the ability to generate interfacial $\beta_{0,sec}$ phase precipitates making this alloy group an ideal candidate for both parent material and braze joint mechanical performance evaluation.

Chapter 3

Material and Experimental Procedures

3.1 Material

3.1.1 Parent Material

A Group B $\beta - \gamma$ TiAl alloy containing Nb and Mo as beta stabilizing elements was utilized as part of this work and is designated “G2”. All consolidation procedures associated with the P/M process were carried out at the National Research Council of Canada. Gas-atomized powders (composition in Table 3.1) with a nominal mesh powder size of -35 were supplied by Crucible Research Inc. The powders were encapsulated in type 304 seamless stainless steel tubes under an argon atmosphere and subjected to a degassing treatment at 230 °C for a minimum of 48 hours under a vacuum of 1×10^{-5} torr. Following the degassing treatment, samples were subjected to a hot isostatic pressing (HIP) treatment in an argon atmosphere (1250 °C/200 MPa/1 hr $\rightarrow$ 1100 °C/200 MPa/3 hr + slow cooling to RT) [40, 41]. Following the HIP treatment, samples were de-canned by machining the HIP’d compacts on a lathe until the stainless steel was removed. After the machining step, samples had an approximate nominal size of 10mm dia by 80 mm in length and were subjected to a step cooled solution heat treatment (SHT) in air (1400 °C/40 min. + FC at 12 °C/min. to 1280 °C + AC to RT) [40, 113].

The resultant microstructure after HIP+SHT (Figure 3.1) is termed “fully lamellar”. Fully dense equiaxed colonies with an α_2/γ lath structure have a diameter of approximately 40 μ m and a volume fraction greater than 99 vol.%. The thickness of the laths within the α_2/γ colonies are on the order of 40 nm, with no evidence of secondary beta phase precipitates ($\beta_{0,sec}$). The α_2/γ colonies are surrounded by a

thin intercolony region containing the γ (dark) and β_0 (bright) phases (Figure 3.1b). The colony boundary morphology is a mix of planar and well interlocked. The specific HIP+SCHT condition was optimized through variation in the $T_{F/A}$ temperature to produce a microstructure exhibiting qualities that may lead to superior creep response [40]. Thus, the specific HIP+SCHT condition was utilized as the starting parent material condition for all diffusion brazing experiments.

For the purpose of structure-property relationship comparison, selected HIP+SCHT samples were given a further aging treatment at 900 °C for 6 hours and 24 hours followed by air cooling. Aging the HIP+SCHT condition coarsens the intercolony $\gamma + \beta_0$ phases at the expense of α_2/γ colonies producing a “near lamellar” microstructure with an α_2/γ lamellar colony fraction on the order of 90 vol.%. Within the α_2/γ colonies, the precipitation of a secondary interfacial beta phase, $\beta_{0,sec}$, occurs at the expense of α_2 lath dissolution (Figure 3.2).

Table 3.1: Nominal Composition of the Beta-Gamma Alloy “G2” (at.%)

Material				
Designation	Ti	Al	Nb	Mo
G2	Bal.	43.54	1.73	1.80

Figure 3.1: G2 parent material microstructure in the SCHT condition at various magnifications (a) BSE-SEM image at 2000x, (b) BSE-SEM image at 8000x, (c) BSE-SEM image of the lath structure at 50000x, (d) edge-on brightfield TEM image of the lath structure

Figure 3.2: G2 parent material in the SCHT + aged condition at 900C/24 hours. (a) BSE-SEM image at 2000x showing the coarsening of the intercolony $\gamma + \beta_0$ phases, (b) BSE-SEM image at 50000x showing lamellar dissolution at the expense of precipitation of an interfacial $\beta_{0,sec}$ precipitate, (c) lamellar interface microstructure under brightfield TEM showing the precipitation of interfacial $\beta_{0,sec}$ precipitates

3.1.2 Braze Interlayer Material

The braze interlayer material utilized as part of this work consisted of a low melting point eutectic braze foil named “TiNi-67” supplied by Wesgo Metals Inc. The TiNi-67 braze foil consists of an amorphous composite interlayer of commercially pure nickel with a nominal thickness of 10 μm , sandwiched between two pieces of commercially pure titanium each with a nominal thickness of 20 μm (Figure 3.3).

Figure 3.3: BSE image of the TiNi-67 braze material [114].

3.2 Procedures

3.2.1 Diffusion Brazing

The diffusion brazing assembly (Figure 3.4) consisted of the following sample preparation procedure. Parent materials were sectioned utilizing a precision diamond saw into button samples of approximately 11 mm diameter by 6 mm thick for diffusion brazing experiments, and 11 mm diameter by 38 mm thick for tensile creep experiments. One face of each sample was mechanically ground utilizing successively finer SiC papers to 800 grit. The braze material was punched to a diameter of approximately 75-90% of the diameter of the parent material samples. Both parent materials

Figure 3.4: Diffusion brazing assembly configuration

and braze materials were cleaned in an ultrasonic bath of acetone for 30 minutes followed by air drying. A butt joint was employed by placing the faying surface of each parent material in contact with the braze interlayer, and a dead weight was placed on the assembly to produce 5.0 ± 0.2 kPa of bonding pressure (See Figure 3.4, Table 3.2, and Figure 3.5). Diffusion brazing was carried out utilizing a Bridgman furnace supplied by Centorr Furnaces Vacuum Industries Inc.. Bonding temperatures ranges from 1030 °C to 1150 °C with isothermal holding times ranging from 30 minutes to 70 minutes under a typical vacuum level of 5×10^{-4} Torr (Table 3.3). Cooling was initiated by turning off the furnace elements which resulted in a cooling rate of 70-90 K/min depending on the isothermal hold temperature.

Figure 3.5: Diffusion brazing button assemblies loaded inside the furnace on a ceramic platform with a dead weight applied to the top surface of each assembly

Table 3.2: Diffusion Brazing Configurations

Layer	C1
PM1	G2-SCHT
L1	—
L2	20 μm - Ti
L3	10 μm - Ni
L4	20 μm - Ti
L5	—
PM2	G2-SCHT

Table 3.3: Boding conditions selected for diffusion brazing experiments

DB			
Test No.	Configuration	Temp (°C)	Time (min)
DB1	C1	1030	30
DB2	C1	1030	50
DB3	C1	1030	70
DB4	C1	1090	30
DB5	C1	1090	50
DB6	C1	1090	70
DB7	C1	1150	30
DB8	C1	1150	50
DB9	C1	1150	70

3.2.2 Post Bond Heat Treatment

Post bond heat treatments were carried out utilizing the same Bridgman furnace as in Section 3.2.1. Samples were placed on the platform inside the hot zone and the heat treatment schedule was carried out under a positive pressure of ultra high purity argon at 5 psi flowing at a rate of 17.5 ft³/hr. All post bond step-cooled heat treatment (PB-SCHT) specimens were subjected to a bond cycle at 1150 °C for 70 minutes. Various PB-SCHT combinations were conducted to homogenize, solutionize, and age the samples (Table 3.4).

Table 3.4: PB-SCHT conditions for diffusion brazing experiments

PBHT	DB		
Test No.	Test No.	PBHT	Aging
PB-SCHT1	DB9	1400/40 → 1280 °C @ 12C/min → FC	–
PB-SCHT5	DB9	1400/40 → 1280 °C @ 12 °C/min → FC	900 °C/6hr → AC
PB-SCHT6	DB9	1400/40 → 1280 °C @ 12 °C/min → FC	900 °C/24hr → AC

3.2.3 Specimen Characterization

Optical Microscopy

For metallographic examination under optical microscopy, samples were transversely sectioned using a precision diamond saw. Samples employing the TiNi-67 foil were mounted in bakelite, while samples employing aluminum interlayers were mounted in epoxy resin and cured at room temperature. Typical grinding and polishing procedures were employed to produce a mirror finish. Photomicrographs were taken under brightfield reflected-light conditions in the as-polished state to elucidate the degree of porosity within the samples. Additionally, selected samples were subjected to a chemical etching treatment to reveal the lamellar colony volume fraction and lamellar colony size. Preliminary lamellar colony volume fraction measurements were conducted utilizing a manual point counting method according to ASTM E562 [115], while preliminary colony size measurements were conducted utilizing a linear intercept method on two-phase structures according to ASTM E1382 [116]. Sample preparation

and analysis was conducted at the National Research Council of Canada, Aerospace Portfolio.

Scanning Electron Microscopy

For metallographic examination under scanning electron microscopy, samples were transversely sectioned using a precision diamond saw followed by mounting in bakelite or epoxy resin as outlined previously. Typical grinding and polishing procedures were employed to produce a mirror finish for bonded samples while an electrochemical polishing procedure was employed for creep samples. Photomicrographs were taken under backscatter-electron mode (BSE) in a PhillipsTM XL30S scanning electron microscope (SEM) equipped with an EDAXTM energy dispersive spectrometry (EDS) detector. Volume fraction measurements of secondary phases within as-crept, as-bonded, and bonded-crept samples were conducted utilizing ASTM E562. EDS spot analysis was conducted to identify the composition and potential phases within the specimens. EDS spot analysis results were compared against the Ti-Al-Ni ternary phase diagram at 900 °C [117], and the Ti:Al ratio on the binary Ti-Al phase diagram [118] for braze samples. EDS line scans were acquired across a line length of approximately 500-600 μm to determine the compositional gradients throughout the braze zone and parent material. Sample preparation and analysis was conducted at the National Research Council of Canada, Aerospace Portfolio.

X-Ray Diffraction Measurements

X-Ray diffraction (XRD) measurements were conducted on a Rigaku Ultima IV Diffractometer on as-bonded specimens to confirm the identity of phases within the bonded samples. The specimens were analyzed in focused beam / continuous scan mode with an X-Ray power level of 40 kV, a scan speed of 0.5 deg/min, a step width of 0.02 deg, and a scan range from 20-90 degrees. Specimens were longitudinally sectioned to approximately 1 mm from the centerline of the bond. Samples were mounted on a precision depth holder and ground to 1200 grit SiC surface finish. XRD analysis was conducted at 800 μm from the centerline of the bond, 50 μm from the centerline of the bond, and 5 μm from the centerline of the bond to identify phases throughout the bond zone. Sample preparation was conducted at the National Research Council of Canada - Aerospace Portfolio, while XRD measurements were conducted at the University of Ottawa X-Ray Core Facility.

Micro Computed Tomography Measurements

Micro computed tomography (micro-CT) measurements of selected bonded and SHT+aged specimens were conducted to determine the severity of porosity within the joint centerline prior to creep testing. A Bruker Skyscan 1173 operating at a voltage of 130 kV and a source current of 61 μ A with a rotation angle of 0.185 degrees was utilized to generate CT scans within a 11mm section of the gauge length containing the joint centerline producing a resolution of 6 x 6 x 6 μ m voxels. A 0.25mm brass filter was utilized to reduce beam hardening artefacts. A relative qualitative comparison of the effect of porosity on creep response was compared for specimens subjected to a constant load creep stress of 140 MPa at 760 °C. Micro-CT measurements were conducted at the Carleton University within the Department of Earth Sciences.

3.2.4 Mechanical Testing

Microhardness

Microhardness measurements were conducted across the braze zone of mounted and polished specimens using a Leco® LM241 micro-vickers hardness tester with a dwell time of 13 seconds and a 50 gf test load (reported as HV0.05). An offset pattern with minimum indent spacing according to ASTM E384 [119] was utilized to generate hardness profiles. Sample preparation and microhardness measurements were conducted at the National Research Council of Canada - Aerospace Portfolio.

Creep

Creep samples were machined at Metcut Research Inc. (Cincinnati, OH) by low stress grinding with a nominal gage length and diameter of 22 mm and 4 mm respectively (Figure 3.6). For diffusion brazed creep specimens, the braze zone was maintained within +/- 1.5 mm of the centerline of the gauge length. Constant load tensile creep tests were performed on both substrate material and bonded+PBHT material in air at 760 °C and 140 MPa, 208 MPa, and 276 MPa (Table 3.5). Creep load was applied instantaneously with strain measurements initiated prior to loading. Creep strain was measured with a linear variable displacement transducer (LVDT) equipped extensometer providing a strain resolution of +/- 1.5×10^{-5} . Details of the creep frame and associated set-up may be found in [120]. Strain measurements were recorded at 1

(a)

(b)

Figure 3.6: Tensile creep specimen dimensions (a), and associated creep sample (b) [120].

second intervals, increasing to a maximum interval of 30 minutes. Heat treated samples were examined by both optical (OM) and scanning electron microscope (SEM). Samples for optical microscopy analysis were sectioned and polished using standard metallographic procedures followed by etching in 25 ml glucose + 12 ml H_2O + 12 ml HNO_3 + 1 ml HF. Samples for SEM analysis were sectioned and electropolished using a 64% methanol + 31% butanol + 5% perchloric acid solution at $-45^\circ C$. Creep experiments were conducted at Carleton University within the Department of Mechanical and Aerospace Engineering.

Table 3.5: Creep conditions for substrate material and diffusion brazing experiments (No DB test number indicates a substrate only test condition).

Creep Test No.	PBHT Test No.	DB Test No.	Solutionizing/PBHT	Aging	Creep Stress (MPa)
CR1	–	–	1400/40 → 1280 °C @ 12C/min → FC	–	140
CR2	–	–	1400/40 → 1280 °C @ 12C/min → FC	–	276
CR3	–	–	1400/40 → 1280 °C @ 12C/min → FC	900 °C/6hr → AC	140
CR4	–	–	1400/40 → 1280 °C @ 12C/min → FC	900 °C/6hr → AC	276
CR5	–	–	1400/40 → 1280 °C @ 12C/min → FC	900 °C/24hr → AC	276
CR6	PB-SCHT1	DB9	1400/40 → 1280 °C @ 12C/min → FC	–	140
CR7	PB-SCHT1	DB9	1400/40 → 1280 °C @ 12C/min → FC	–	208
CR8	PB-SCHT1	DB9	1400/40 → 1280 °C @ 12C/min → FC	–	276
CR9	PB-SCHT1	DB9	1400/40 → 1280 °C @ 12C/min → FC	–	276
CR10	PB-SCHT5	DB9	1400/40 → 1280 °C @ 12C/min → FC	900 °C/6hr → AC	140
CR11	PB-SCHT5	DB9	1400/40 → 1280 °C @ 12C/min → FC	900 °C/6hr → AC	140

Chapter 4

Characterization of As-Bonded TiNi Joints

In the following chapter, the morphology and dynamics of both the interfacial bond zone microstructure and parent material microstructure are characterized during isothermal solidification of TiAl/TiNi-67/TiAl diffusion couples at 1030 °C, 1090 °C, and 1150 °C for isothermal solidification times ranging from 30 minutes to 70 minutes. Additionally, the kinetics of the growth of the various microstructural regions within the braze zone are elucidated, and the structure-property relationships associated with the braze zone are characterized in terms of microhardness property evaluation.

4.1 1030 °C Bonding Temperature Microstructure

The sequence of formation of the phases within the braze zone are identified by evaluating the diffusion/solidification path on the Ti-Al-Ni ternary phase diagram at the bonding temperature (1027 °C - Figure 4.2a). The dashed line 1-5 in Figure 4.2a represents the joining of the end member compositions (i.e. parent material and liquid braze) prior to dissolution of the parent material, and the solid line 1-2-3-4-5 represents the possible diffusion path associated with the phases found within the solidified braze zone prior to the end of the isothermal holding stage. The phases associated with cooling of the residual liquid and those phases associated with the diffusion zone are evaluated against the 900 °C Ti-Al-Ni phase diagram (Figure 4.2b) based on energy dispersive spectroscopy (EDS) spot analysis of each contrasting phase under back-scatter electron (BSE) scanning electron microscopy imaging. Since each

spot contains 5 measured constituents (namely Ti, Al, Nb, Mo, and Ni), EDS spot analysis results were re-normalized based on the data associated with Ti, Al, and Ni for comparison against the ternary Ti-Al-Ni phase diagram at 900 °C.

For the 1030 °C TLP experiment, the resultant bonded microstructure is divided into three zones for convenient phase identification (Figure 4.1a). Within zone 1, SEM-BSE imaging reveals a semi-continuous dark phase A that is elongated parallel to the bondline, and two globular phases B, and C (Figure 4.1b). These phases represent $\alpha_2 - Ti_3Al$, $\beta(\beta_0) - Ti$, and $\tau_3 - TiNi_{0.5}Al_{1.5}$ phases respectively with the possible precipitation of an additional phase within the τ_3 phase based on SEM-EDS spot analysis (Table 4.1).

Table 4.1: Summary of EDS spot analysis on the 1030 °C / 30 min condition

Zone No.	Phase No.	Ti (at%)	Al (at%)	Nb (at%)	Mo (at%)	Ni (at%)	Ti/Al Ratio	Possible Phases
1	A	61.5	28.0	0.8	0.4	0.7	2.2	α_2
	B	54.8	31.9	1.1	1.5	3.2	1.7	β
	C	33.7	37.1	0.6	0.2	19.9	0.9	$\tau_3 + \text{ppt}$
2	D	55.4	33.0	1.1	0.9	1.6	1.7	α_2
	E	53.2	33.1	1.4	1.6	2.3	1.6	β
	F	37.3	38.1	0.9	0.5	15.4	1.0	$\tau_3 + \text{ppt}$

Above the melting point of the braze foil (980 °C), the binary Ti-Ni liquid achieves equilibrium with the parent material through a two-stage process. First, when the liquid braze comes in contact with the parent material, dissolution of the parent material will occur into the melt. By dissolving the parent material into the melt, Al, Ti, Nb, and Mo concentrations in the melt will increase. When Al dissociates to the liquid from both the $\gamma + \alpha_2$ phases, the Al enriched liquid reacts with the parent material to form a semi-continuous α_2 -Ti₃Al phase (A) at the solid/liquid interface whereby $TiAl_{(S)} + 2Ti_{(L)} \rightarrow Ti_3Al_{(S)}$. The identical reaction has been found for similar bonding scenarios utilizing TiNi and conventional γ -TiAl substrates [82, 84], and is supported by the lack of beta stabilizing elements and hence stoichiometric nature of the resultant composition of phase A (schematically represented by point 2 in Figure

4.2a). This reaction preferentially consumes Ti from the liquid, resulting in a further increase in Al enrichment within the liquid (line 5-4 in Figure 4.2a) until such time that equilibrium is reached between the liquid and the growing stoichiometric phase A.

Once the interfacial reaction producing phase A (α_2 -Ti₃Al) has completed, it is postulated that the scalloped phase B ($\beta(\beta_0)$ -Ti) grows during isothermal solidification by achieving tie-line equilibrium with the liquid phase at the bonding temperature (line 3-4 in Figure 4.2). Under such growth conditions, phase B contains higher levels of Ni, Nb, and Mo elements compared with phase A due to the increased solubility of these elements in the solidifying β -Ti phase compared with the stoichiometric reaction mechanism proposed for the formation of phase A. Figure 4.2a reveals that the β -Ti region has a Ni solubility limit dependent on the Ti/Al concentration ratio that increases with increasing Al content, and has a significant range varying from 0 at.% Ni at Ti-12Al (at.%) up to 30 at.% Ni at Ti-38Al (at.%). Phase B nucleates from the phase A / liquid interface and grows towards the centerline of the joint from both substrates. Phase B scallops have a broad cellular morphology and generally contact each other across the bondline due to the advancing dual solidification fronts, leaving small pockets of nickel rich liquid (phase C - Figure 4.1b). The contact point of the advancing phase B scallops do not occur at the vertical crest of each cell, but shift their growth pattern to consume the remaining liquid resulting in a misaligned growth pattern. Additionally, due to the semi-continuous nature of phase A, short circuit diffusion pathways exist at the zone 1/2 interface between the residual liquid and phase E of zone 2 (arrows in Figure 4.1b). The short circuit path allows a flux of Ni into zone 2, with a mutual flux of Al or Ti into the liquid. These mutual fluxes likely result in a limitation of the potential shift in equilibrium tie-line composition at the solid/liquid interface to a region associated with the broad two phase L+ β region.

The formation of phase C is likely due to the cooling of residual liquid that results in the $L \rightarrow \tau_3$ transformation. This transformation is supported by the wide homogeneity range and existence of τ_3 which exists at a minimum temperature of 1000 °C [121] and encompasses the measured composition of phase C based on the Ti-Al-Ni phase diagram at 900 °C (Figure 4.2b). Within phase C, the potential for τ_4 precipitation is possible and dependent on changes in Ni solubility within the τ_3 phase as the temperature decreases at the end of the bonding cycle. Further confirmation of

the residual liquid transformation may be assessed through TEM evaluation, as well as via a mathematical model of non-equilibrium solidification based on the liquidus projection of the ternary Ti-Al-Ni phase diagram [122]. Such an evaluation will be the focus of future work.

Within zone 2, SEM-BSE imaging reveals two elongated phase D and E with a globular phase F (Figure 4.1c). These phases represent the α_2 , β , and τ_3 phases respectively based on SEM-EDS spot analysis (Table 4.1). All three phases in zone 2 are finer than those found in zone 1, and the morphology of phases D and E appear to be influenced by the orientation of the adjacent fully lamellar microstructure of the parent material in zone 3.

For zone 2, it is postulated that the formation of all three phases occurs due to solid state transformations. The combined preferential dissolution of Al at the beginning of isothermal hold temperature, along with the existence of short circuit pathways in the advancing isothermal growth front result in an Al depletion, and Ni enrichment in zone 2. A consequence of the depleted Al content and Ni enrichment within zone 2 is the transformation of the dual phase $\alpha_2 + \gamma$ lamellar structure to a tri-phase $\alpha_2 + \beta + \tau_3$ coarsened structure with an orientation similar to prior α_2/γ colonies. At the interface between zone 2 and zone 3, the Al content sharply decreases at the expense of the Ti content, while the Ni content increases more gradually from the zone 2/3 interface into zone 2 as shown by the EDS line scan in Figure 4.3a. As both phase D and E coarsen during isothermal solidification simultaneously within zone 2, the Ni concentration gradient across the braze zone promotes the diffusion of Ni into zone 3 from zone 2 and zone 1. The resulting increase in Ni content in zone 2 leads to Ni rich α_2 phases in zone 2 with a Ni composition on the order of 4 at.%. During cooling, the Ni solubility limit within the α_2 phase decreases to approximately 1 at.%, resulting in the precipitation and coarsening of a fine globular τ_3 phase (phase F - Figure 4.2b) within zone 2. The lower Ni content of the τ_3 phase in zone 2 compared with zone 1 may be due to the difficulty in resolving the τ_3 phase by the EDS detector due to the finer morphology.

Evaluating the parent material microstructure, at the zone 2/3 interface, a sharp morphological change is evident from a fully lamellar α_2/γ colony in zone 3 to a coarsened $\alpha_2 + \beta_0 + \tau_3$ three phase structure in zone 2. Within the proximity of the zone 2/3 interface, inside the lamellar colonies, evidence of interfacial precipitation of

an additional phase on existing α_2 laths is present (Figure 4.4). Measured EDS line scans (Figure 4.3 in the zone 3 region adjacent to the zone 2/3 interface) indicate a composition of 2.2 at.% Mo, 2.3 at.% Nb, and between 0.3-0.6 at.% Ni. Since the Nb/Mo contents are at the nominal composition, the additional Ni content will further stabilize the beta phase leading to the likelihood that the interfacial precipitates are the $\beta_{0,sec}$ phase.

(a)

(b)

(c)

Figure 4.1: BSE-SEM images of the 1030 °C/30 minute bonded microstructure with zone locations; Zone 1: Central Region, Zone 2: Diffusion Region, Zone 3: Parent Material (a) Overall microstructure, (b) Zone 1 microstructure, (c) Zone 2 microstructure.

Figure 4.2: (a) Possible diffusion pathway associated with reactive isothermal solidification at the bonding temperature of 1030 °C, (b) SEM-EDS point analysis for zone 1 and zone 2 phases plotted on the ternary Ti-Ni-Al phase diagram at 900 °C.

(a)

(b)

Figure 4.3: EDS line scans of the 1030 °C/30 minute case indicating the (a) Ti/Al/Ni composition profiles and (b) Ni/Nb/Mo composition profiles

Figure 4.4: SEM-BSE image of the zone 2/3 region for the 1030 ° C / 30 minute experiment showing the existence of an interfacial precipitate phase within the lamellar colony

4.1.1 Effect of Isothermal Holding Time on Bondline Microstructure

EDS line scans and SEM-BSE micrographs (Figure 4.5) confirm the lack of significant compositional, microstructural, and zone width variation with holding time for the 1030 °C bonding temperature. Stability of the braze zone is likely due to:

1. The growth rate of scalloped phase reduces with reduced interfacial energies. As the scallops coalesce, there is a reduction in short circuit pathways to zone 2 and diffusion is relied upon through the stoichiometric α_2 phase.
2. The stoichiometric α_2 phase present at the zone 1/2 interface that partially impedes Ni diffusion away from the centerline of the bond.
3. The low diffusivity of the participating species in the γ and α_2 phases (on the order of 1×10^{-14} m²/s) at the 1030 °C bonding temperature.
4. The starting ternary composition of the liquid and the contrast between diffusing species within the solid may result in limited solid/liquid interface progression at longer isothermal holding times [68].

Different mechanisms occur during heating, the isothermal hold segment, and on cooling. A schematic representation (Figure 4.6) of the potential sequence of reactions and mechanisms associated with diffusion brazing $\beta - \gamma$ TiAl alloy at 1030 °C are proposed:

1. Melting of the Ti-24Ni (at.%) braze alloy in the range 980-1030 °C.
2. Dissolution of Ti, Al, Nb, and Mo from the parent material into the molten braze alloy resulting in a depleted Al interdiffusion zone of primarily $\alpha_2 + \beta_0$.
3. Reactive diffusion at the solid/liquid interface producing a near stoichiometric, semi-continuous α_2 phase through the reaction $\text{TiAl}_{(S)} + 2\text{Ti}_{(L)} \rightarrow \text{Ti}_3\text{Al}_{(S)}$.
4. Isothermal solidification of a scalloped β phase via a tie-line between the liquid and the β phase at 1030 °C.

5. Transformation of fine $\gamma + \alpha_2$ lamellar colonies to a coarsened $\beta + \alpha_2$ microstructure with a similar orientation as the prior α_2/γ lamellar colonies within the diffusion zone.
6. On cooling, transformation of the remaining residual liquid at the centerline of the joint to τ_3 .
7. On cooling, precipitation and growth of the τ_3 phase in the interdiffusion zone due to reduced Ni solubility in the $\alpha_2 + \beta$ phases.

Figure 4.5: SEM-BSE images and associated EDS line scans for the 1030 °C bonding case at (a-b) 30 minutes, (c-d) 50 minutes, and (d-e) 70 minutes isothermal solidification time. Line in (a) indicates typical line scan orientation for all subsequent EDS line scan analysis.

Figure 4.6: Proposed diffusion brazing process associated with TiAl/TiNi67/TiAl diffusion brazing at 1030 °C for 30 minutes

4.2 1090 °C Bonding Temperature Microstructure

For the 1090 °C TLP experiments, the division of each zone is shown in Figure 4.7a. Within zone 1, EDS analysis reveals three globular phase A, B, and C (Figure 4.7b). These phases represent α_2 , β , and τ_3 phases respectively (Table 4.2). It is postulated that the phases within zone 1 formed via the same mechanisms as the 1030 °C TLP experiment. However, within phase B and phase C, there appears to be a very fine bright precipitate that was not evident in the 1030 °C experiments.

Table 4.2: Summary of EDS spot analysis on the 1090 °C/30 minute condition

Zone	Phase	Ti	Al	Nb	Mo	Ni	Ti/Al	Possible
No.	No.	(at%)	(at%)	(at%)	(at%)	(at%)	Ratio	Phases
1	A	62.8	28.5	0.4	0.3	0.5	2.2	α_2
	B	54.4	30.9	0.8	0.9	3.6	1.8	β +ppt
	C	33.0	35.3	0.2	0.1	20.5	0.9	τ_3 +ppt
2	D	53.7	35.1	1.2	0.7	0.8	1.5	α_2
	E	52.8	33.8	1.2	1.4	2.3	1.6	β +ppt
	F	40.2	39.0	1.2	1.1	10.2	1.0	τ_3

Within zone 2, EDS analysis reveals three fine phases D, E, and F which appear to be influenced by the fully lamellar structure of the adjacent parent material. (Figure 4.7c). These phases represent α_2 , β , and τ_3 phases respectively (Table 4.2). It is believed that phase D, E, and F all form via similar mechanisms as the zone 2 phases found in the 1030 °C TLP experiments. Phase F is finer and accicular in nature compared with phase D and E, and appears to form at prior lamellar colony boundaries as well as within the phase E matrix.

For the 1090 °C experiment, the τ_3 volume fraction has increased in zone 1 and depleted in zone 2 compared with the 1030 °C experiment. No ternary Ti-Al-Ni phase diagram is available in the literature at the bonding temperature, however it is postulated that the liquid phase field continues to extend to higher Al content. This extension in the liquid phase field results in greater growth of the liquid interlayer during dissolution of the parent material leading to a greater zone 2 width.

Immediately adjacent to the zone 1/2 interface lies a single α_2 phase with similar composition and morphology as that found at the 1030 °C bonding condition. It is postulated that this α_2 phase forms via a similar reaction as the 1030 °C bonding condition. The scalloped β phase that growth during isothermal solidification via the same mechanism as the 1030 °C bonding condition contains a small white precipitate embedded within the β matrix that may be either τ_3 or τ_4 . EDS spot analysis on this precipitate region is inconclusive due to the fine size, however the composition of this precipitate phase contains an Al content similar to the surrounding matrix, with an increase in Ni content that suggest a shift towards the τ_3 phase field. In addition to the fine precipitates within zone 1, Figure 4.7c reveals the larger acicular nature of the white phase near the boundary between zone 3 and zone 2, which does not exist for bonding experiments conducted at 1030 °C. For this white precipitate to occur, a reaction within the α_2 phase near the zone 2/3 interface may occur due to supersaturation of β stabilizing elements within the α_2 matrix producing either a fine acicular β_0 phase or a nickel rich intermetallic compound such as τ_3 .

The increased acicular precipitation of the white phases within both zone 1 and zone 2 for the 1090 °C experiment over the 1030 °C experiment may be due to increased solubility of Ni in the α_2 phase at the 1090 °C bonding temperature. At 1090 °C, greater solubility of Ni in the α_2 phase results in greater growth of a single α_2 phase with higher Ni content, and little to no globular growth of the τ_3 phase. On cooling from 1090 °C, a precipitation reaction within the α_2 phase may occur due to supersaturation of Ni within the α_2 matrix producing fine acicular precipitates.

Features in the parent material associated with the 1030 °C bonding condition are also evident at the 1090 °C bonding condition. As with the 1030 °C condition, at the zone 2/3 interface, a sharp morphological change is evident from a fully lamellar α_2/γ colony in zone 3 to a coarsened $\alpha_2+\beta+\tau_3$ three phase structure in zone 2. Within the proximity of the zone 2/3 interface, inside the lamellar colonies, evidence of interfacial precipitation of an additional phase on existing α_2 laths is present (Figure 4.7c). EDS line scans (Figure 4.10b) indicate a composition of 2.0 at.% Mo, 2.0 at.% Nb, and 0.5 at.% Ni penetrating 10 μm inside zone 3 at the zone 2/3 interface. Since the Nb/Mo contents are at the nominal composition, the additional Ni content will further stabilize the beta phase leading to the likelihood that the interfacial precipitates are the β_0 phase.

(a)

(b)

(c)

Figure 4.7: BSE-SEM images of the 1090 °C/30 minute bonded microstructure with zone locations; Zone 1: Central Region, Zone 2: Diffusion Region, Zone 3: Parent Material (a) Overall microstructure, (b) Zone 1 microstructure, (c) Zone 2 microstructure

Figure 4.8: EDS spot results from Table 4.2 plotted on the 900C Ti-Al-Ni phase diagram.

4.2.1 Effect of Isothermal Holding Time on Bondline Microstructure

With increased bonding time at 1090 °C, a number of microstructural differences are evident between the three holding times (Table 4.3 and Figure 4.9). First, within zone 1, the medium grey scalloped β phase appears to contain both bright and dark precipitates for the 30 minute specimen, while the 50 and 70 minute specimen appear to contain a single β scalloped phase. Second, within zone 2 (Figure 4.9b,d,f), the denuded β phase region adjacent to the zone 1/2 interface contains reduced fine bright precipitates at the 50 and 70 minute holding times compared with the 30 minute holding time. Third, the globular bright phase within zone 2 does not exist at the 30 minute holding time, but is present for both the 50 and 70 minute holding times. The bright globular phase in zone 2 for the 50 and 70 minute specimens appear to congregate primarily around low aspect ratio grains of the α_2 phase. When the α_2 phase has a high aspect ratio, the precipitate phase appears embedded in the brighter β matrix with an acicular morphology. Fourth, within zone 2, the bright acicular precipitates near the zone 2/3 interface appear to reduce in volume fraction for the 50 and 70 minute holding times. Fifth, an elongated dark phase is evident for the 50 and 70 minute holding times (indicated by arrows in Figure 4.9d, and Figure 4.9f), which based on EDS point analysis, contains Ti-44.5Al-1.4Nb-1.1Mo-1.7Ni (at.%) and is compositionally consistent with the γ phase. The addition of the γ phase appears likely via one of two mechanisms;

1. An $\alpha_2 \rightarrow \gamma$ or $\beta \rightarrow \gamma$ transformation occurs within zone 2 with increased isothermal holding time.
2. An incomplete $\gamma \rightarrow \alpha_2$ transformation during the dissolution process which results in retained γ phase from the parent material within the diffusion zone that coarsens during the isothermal holding time.

In either mechanism, with increased holding time, the Al concentration homogenizes across the bond and is evident by the slight average increase in Al concentration with isothermal holding time from 36.3 at.%Al at 30 minutes to 39.3 at.% Al at 70 minutes respectively (Figure 4.10b,f). With increasing homogenization of Al, the γ phase volume fraction continues to increase within the diffusion zone. With increased γ growth the potential for nickel rich phases increases due to slightly reduced solubility

of Ni in the γ phase compared with α_2 phase at the bonding temperature. The significantly reduced solubility of the γ phase compared with the β phase at the bonding temperature based on the ternary phase diagram at 1027 °C, leads to a rejection of Ni to the γ/α_2 or γ/β interfaces.

Table 4.3: Microstructural features associated with different isothermal holding times at 1090 °C

Zone	Microstructural			
	Feature	30	50	70
1	τ_3 with bright substructure	++	++	++
1	Scalloped β with bright and dark ppt's	++	-	-
1	Dark semi-continuous α_2 phase	++	++	++
2	Denuded β phase with bright ppt's	++	+	+
2	Globular bright phase	-	++	++
2	Acicular bright phase near zone 2/3 interface	++	+	+
2	Elongated γ phase near zone 2/3 interface	-	+	++

X-Ray diffraction (XRD) was performed on the 1090 °C / 70 minute condition to further confirm the identify of phases within the different regions of the joint. The 1090 °C / 70 minute condition was selected due to the greatest evolution of the varying phases within the joint. It is assumed in this XRD analysis that the phases found at the 1090 °C / 70 minute condition correspond with the phases found at the 1030 °C bonding condition where composition and morphology of major phases are consistent between the two bonding conditions. Figure 4.12 shows three XRD patterns of the 1090 °C / 70 minute condition with approximate surface scan positions marked in Figure 4.11. In the parent material (Figure 4.12a), three phases can be clearly distinguished (i.e. α_2 , γ , and β_0). The single peak at $2\Theta = 39^\circ$ contains the complete overlapping response of the $\alpha_2(002)$ and $\gamma(111)$ reflections. The XRD pattern near the diffusion zone (Figure 4.12b) indicates the presence of a fourth phase due to the additional peaks at a 2Θ angle of 42, 43, and 81 degrees. This fourth phase is identified as the τ_3 -Ti₂NiAl₃ phase (hexagonal C14, P6₃/mmc, MgZn₂) laves phase with lattice parameters of approximately $a = 5.003 \text{ \AA}$ and $c = 8.041 \text{ \AA}$. Along with

the additional τ_3 phase found in the diffusion zone, an increase in α_2 and β_0 phases has occurred in the diffusion zone with a possible reduction in γ phase volume fraction.

Near the centerline of the joint (Figure 4.12c), the XRD pattern indicates a phase mixture of primarily α_2 , β_0 , and τ_3 phases with significantly reduced γ phase. The reduction in γ phase is evident by the complete elimination of the γ -(001), (110), (200), (201), and (112) reflections, with only trace reflections at $2\Theta = 35, 44, 78$ and 79 degrees. Additionally, a lattice shift is noticed for the τ_3 peaks to lower 2Θ values. The significant homogeneity range of the τ_3 phase offers a variation in lattice spacing due to the unique site preference of the Ti, Al, and Ni atoms with composition afforded by this phase. Lattice spacings/ratios have been measured within a range of $a = 4.9956\text{-}5.015 \text{ \AA}$, $c=8.0383\text{-}8.2249 \text{ \AA}$, and $c/a=1.6087\text{-}1.6440$ [117]. Both the τ_3 phase in the diffusion zone and central zone fall within the above lattice spacing range, and the variation is likely due to the difference in composition between the τ_3 phases in the various regions of the joint.

The central zone and diffusion zone XRD pattern were evaluated against additional Ti_2Ni , NiAl , τ_1 , τ_2 , and τ_4 phases as the bright substructure shown in phase 1 of the central zone may be due to Ti_2Ni or τ_4 precipitation on cooling [121], and the different morphological bright phases in the diffusion zone (i.e. acicular versus globular) may in fact be phases other than τ_3 . In both the diffusion zone and central zone, line matching indicated no evidence of the Ti_2Ni , τ_2 or τ_4 phases within the joint. However, weak peak locations associated with the τ_1 and NiAl phase are possibly overlapping the β_0 reflections due to similar cubic lattice structures and lattice spacings between these three phases. Reflections at $2\Theta = 44.3^\circ$ and 81° initially associated with the τ_3 phase are somewhat stronger than expected based on the intensity ratios with the main τ_3 reflections at 42.2° and 42.9° . However, texture effects may support the association of these peaks with the τ_3 phase. On the other hand, if the $2\Theta = 44.3^\circ$ and 81° reflections are associated with the τ_1 phase then stronger τ_1 reflections must occur at $2\Theta = 39$ and 72° which are located within both the diffusion zone pattern and the central zone pattern, overlapping with the β_0 reflections. If the $2\Theta = 44.3^\circ$ and 81° reflections are associated with the NiAl phase, then these would in fact be the strongest peaks associated with the NiAl phase. In any instance, if these trace reflections are associated with the NiAl or τ_1 phases, their volume fractions are less than 1 vol.% and are not evident within typical SEM-BSE micrographs. In order

to confirm the existence of an additional precipitate phase within the microstructure, additional characterization utilizing either high resolution SEM composition/phase maps, EBSD, or TEM is required.

Figure 4.9: SEM-BSE images for the 1090 °C bonding case at (a-b) 30 minutes, (c-d) 50 minutes, and (e-f) 70 minutes isothermal solidification time. Arrows indicate both dark and bright precipitates within the primary β phase.

Figure 4.10: SEM-BSE images and associated EDS line scans for the 1090 °C bonding case at (a-b) 30 minutes, (c-d) 50 minutes, and (e-f) 70 minutes isothermal solidification time

Figure 4.11: Approximate location of XRD scans conducted on the 1090 °C / 70 minute specimen. The parent material scan was taken approximately 800 μm from the centerline of the joint and the location is out of the field of view of the SEM-BSE micrograph.

Figure 4.12: X-ray diffraction patterns for the 1090 °C / 70 minute specimen at (a) 800 μm away from the centerline of the joint, (b) 60 μm away from the centerline of the joint near the diffusion zone, and (c) 10 μm away from the centerline of the joint.

4.3 1150 °C Bonding Temperature Microstructure

For the 1150 °C TLP experiment, the microstructure is divided into three zones for convenient phase identification (Figure 4.13a). Within zone 1, EDS analysis reveals three phases A, B, and C (Figure 4.13b). These regions represent γ , α_2 , and $\beta+\tau_3$ phases respectively (Table 4.4, Figure 4.14).

Table 4.4: Summary of EDS spot analysis on the 1150 °C/30 condition

Zone	Phase	Ti	Al	Nb	Mo	Ni	Ti/Al	Possible
No.	No.	(at%)	(at%)	(at%)	(at%)	(at%)	Ratio	Phases
1	A	47.4	40.4	1.0	1.2	1.3	1.2	γ
	B	50.8	36.8	0.9	0.6	0.9	1.38	α_2
	C	52.5	33.7	1.1	1.9	2.4	1.56	$\beta_0 + \tau_3$
2	D	46.0	42.3	1.2	1.0	1.4	1.09	γ
	E	50.8	37.0	1.2	0.7	0.8	1.4	α_2
	F	49.0	34.5	1.4	1.8	4.1	1.42	$\beta_0 + \tau_3$

Within zone 1, it is postulated that the continuous α_2 phase (B) forms first via a mechanism whereby preferential dissolution of Al occurs into the liquid such that the parent material exhibits a phase transformation that produces a solid solution α -Ti phase with a disordered HCP crystal structure containing approximately 60 % Ti and 40 % Al with very little alloying elements. Evaluating the Ti-Al-Ni phase diagram at the bonding temperature (Figure 4.15), such a phase exists between the α_2 and γ phases with a composition range of approximately 37-40 at%Al and a Ti/Al ratio range of 1.52-1.70 at 1150 °C [118]. As the parent material depletes in Al to form the continuous α -Ti layer (line 1-2 in Figure 4.15), equilibrium between the liquid phase and the solid is likely reached through a tie-line connection between the liquid and β phase (line 3-4 in Figure 4.15). As the liquid is consumed, the kinetics of the process will dictate the remaining phase formation, with three possible outcomes. Firstly, if equilibrium is maintained between the liquid and β phase, the consumption of the liquid may not significantly shift the equilibrium tie-line away from the L+ β phase field, with a potential tie-line shift to the right due to increased Ni content in the

liquid producing an enriched Ni β phase towards the centerline of the bond. Secondly, if the Al concentration continues to increase within the liquid, the possibility exists for equilibrium conditions at the interface to shift the tie-line to the left and meet the three phase tie triangle encompassing the $L + \alpha_2 + \beta$ phase field. Under such a scenario, α_2 phase formation is likely at the centerline of the bond before cooling, and would contain an Ni content on the order of 2-3 at.% Ni. Thirdly, a scenario exists where equilibrium solidification continues to produce the α_2 phase, and shift the tie-line to even higher Al and Ni content until equilibrium is reached with the three phase $\alpha_2 + \gamma + L$ phase field. Based on the EDS results in Table 4.4, the micrographs in Figure 4.13, and the EDS line scan shown in Figure 4.18a, it appears as though scenario #1 is the likely mechanism due to the significant volume fraction of the β phase (C) present in the microstructure within zone 1, an Al content consistent with a value near the liquidus isotherm on the order of 37 at.% Al present in the centerline of the bond, and a Ni content on the order of the solubility limit of Ni in the β phase at the solidus isotherm. It is postulated that the continuous α -Ti phase (B) layer eventually transforms via a solid state reaction, $\alpha \rightarrow \alpha_2$, on cooling.

One caveat associated with this scenario selection is the existence of the semi-continuous γ phase (A) present primarily at the α/β interphase in zone 1. For beta stabilizing titanium aluminides, equilibrium exists between $\gamma + \beta$ for compositions high in beta stabilizing elements and low in aluminum content. The possibility exists that the Ti-Al-Ni phase diagram available at 1150 °C does not adequately represent the impact of the additional Nb and Mo constituents on the equilibrium phase fields. A high likelihood exists that the β phase is extended to higher Al content allowing for a two phase $\gamma + \beta$ phase field to exist during isothermal solidification, resulting in the growth of the γ phase within zone 1.

The higher bonding temperature of 1150 °C and presence of phase B in zone 1 appears to contribute to accelerated solidification kinetics within the overall braze zone. Self-diffusion is significantly enhanced in α -Ti due to the open HCP structure, and increased levels of impurities such as Ni which diffuse through an interstitial mechanism to promote self-diffusion of both Ti and Al [123]. The accelerated self-diffusion, as well as the fast interstitial diffusion mechanism of Ni in the α -Ti phase, promotes homogenization across the bond zone during isothermal solidification compared with an ordered α_2 or γ phase. The greater homogenization results in complete solidification of the $\beta + \gamma$ phases to the centerline of the joint, eliminating any residual

liquid on cooling, resulting in the elimination of the globular nickel rich τ_3 phase from zone 1. The resulting EDS line scan (Figure 4.18b) for the 1150 °C / 30 minute case reveals a maximum Ni content within zone 1 of approximately 4 at.%Ni compared with 16 at.%Ni and 22 at.%Ni for the 1030 °C / 30 and 1090 °C / 30 minute conditions respectively. Within zone 2, increased γ volume fraction (phase D) occurs throughout the braze zone, and the greater homogenization results in the elimination of the globular τ_3 phase. A schematic of the diffusion brazing process at 1150 °C is shown in Figure 4.16.

Morphological differences are present for the 1150 °C TLP experiment compared with the 1030 °C and 1090 °C TLP experiments. First, the dark γ phase within both zone 1 and zone 2 was not evident in the 1030 °C TLP experiments, and only beginning to form in the 1090 °C TLP experiment near the zone 2/3 interface. Second, the bright globular phase evident in zone 2 (phase F) for the 1030 °C and 1090 °C TLP experiments is non-existent at 1150 °C. Only a small white precipitate phase is evident with a composition consistent with the τ_3 phase (i.e within phase C). Additionally, the γ phase that appears in zone 2 near the zone 1/2 interface for the 1150 °C condition appears to have a random columnar type morphology. The formation of this columnar morphology has been observed in prior work where it was suggested to form by nucleation from a continuous α layer at 1150 °C or on a continuous α_2 layer at lower bonding temperatures [82]. It is likely in this experiment, that the random columnar formation is consistent with nucleation from the α -Ti phase, as the α -Ti phase is likely present in continuous form at the zone 1/2 interface at the higher bonding temperature of 1150 °C.

At the zone 2/3 interface, the fully lamellar α_2/γ colonies are interspersed with a cellular $\gamma + \beta_0$ region as a result of coarsening of the fully lamellar microstructure at the bonding temperature of 1150 °C (Figure 4.17). The EDS line scans (Figure 4.18) reveal a more gradual composition gradient near the zone 2/3 interface which is likely due to the intermixed region of fully lamellar α_2/γ colonies and globular $\gamma + \beta_0$ growth. Within the proximity of the zone 2/3 interface, inside the α_2/γ lamellar colonies, evidence of interfacial precipitation of an additional phase on existing α_2 laths is present (Figure 4.17) with a similar morphology as the 1030 °C and 1090 °C conditions. EDS line scans (Figure 4.18b) indicate a composition of 2.2 at.% Mo, 1.9 at.% Nb, and 0.4 at.% Ni penetrating 15-20 μm inside zone 3 at the zone 2/3 interface. Since the Nb/Mo contents are at the nominal composition, the additional Ni

content will further stabilize the β_0 phase leading to the likelihood that the interfacial precipitates are the β_0 phase.

(a)

(b)

(c)

Figure 4.13: BSE-SEM images of the 1150 °C/30 minute bonded microstructure with zone locations; Zone 1: Central Region, Zone 2: Diffusion Region, Zone 3: Parent Material (a) Overall microstructure, (b) Zone 1 microstructure, (c) Zone 2 microstructure

Figure 4.14: EDS spot results from Table 4.4 plotted on the 900C Ti-Al-Ni phase diagram.

Figure 4.15: Possible diffusion pathway associated with reactive isothermal solidification at the bonding temperature of 1150 °C

Figure 4.16: Proposed diffusion brazing process associated with TiAl/TiNi67/TiAl diffusion brazing at 1150 °C for 30 minutes

Figure 4.17: SEM-BSE image of the zone 2/3 region for the 1150 °C 30 minute experiment showing the existence of an interfacial precipitate phase within the lamellar colony, and the globular $\gamma + \beta_0$ growth within the zone 3 region

4.3.1 Effect of Isothermal Holding Time on Bondline Microstructure

Evident in the EDS line scans (Figure 4.18) is a slight reduction in the Ti and Al composition gradient across the braze zone as isothermal holding time increases from 30 minutes to 70 minutes at 1150 °C. Additionally, the Ni content remains relatively stable near the centerline of the joint, with a slight increase in the bright Ni rich intermetallic phase as isothermal holding time increases. The increase in Ni content is likely a result of the continued growth of the nickel rich τ_3 phase present in both zone 1 and zone 2, indicating that nickel possibly partitions from β to τ_3 with increasing holding time at 1150 °C (Figure 4.19).

XRD was performed on the 1150 °C / 70 minute condition to further confirm the identify of phases within the different regions of the joint. Figure 4.21 shows three XRD patterns of the 1150 °C / 70 minute condition with approximate surface scan positions marked in Figure 4.20. In the parent material (Figure 4.21a), three phases can be clearly distinguished (i.e. α_2 , γ , and β_0). The single peak at $2\Theta = 39^\circ$ contains the complete overlapping response of the $\alpha_2(002)$ and $\gamma(111)$ reflections as was the case for the 1090 °C condition. The XRD pattern near the diffusion zone (Figure 4.21b) is similar in response as the parent material with no indication of a fourth phase. However, volume fractions within the diffusion zone appear to increase in β_0 and α_2 at the expense of the γ phase as indicated by the increase in β_0 -(110), (211), and α_2 -(202) reflections, with a mutual decrease in γ -(001),(002),(200),(201),(113), and (311) reflections respectively.

Near the centerline of the joint (Figure 4.21c), the XRD pattern indicates a phase mixture of primarily α_2 , and β_0 phases. The γ phase is also evident in the centerline of the joint with a reduced volume fraction compared with the diffusion zone based on the elimination of the γ -(001) reflection and a slight reduction in the γ -(112) and (222) reflections. In addition to the three primary phases, the presence of a fourth phase is evident due to the additional trace reflections at a 2Θ angle of 42, 43, and 81 degrees. This fourth phase is identified as the τ_3 -Ti₂NiAl₃ phase (hexagonal C14, P6₃/mmc, MgZn₂) laves phase with lattice parameters of approximately $a = 5.003 \text{ \AA}$ and $c = 8.041 \text{ \AA}$.

Figure 4.18: SEM-BSE images and associated EDS line scans for the 1150 °C bonding case at (a-b) 30 minutes, (c-d) 50 minutes, and (d-e) 70 minutes isothermal solidification time

Figure 4.19: SEM-BSE images for the 1150 °C bonding case at (a-b) 30 minutes, (c-d) 50 minutes, and (e-f) 70 minutes isothermal solidification time (micrographs (a), (c), (e) are zone 1, and micrographs (b), (d), (f) are zone 2).

Figure 4.20: Approximate location of XRD scans conducted on the 1150 °C / 70 minute specimen. The parent material scan was taken approximately 800 μm from the centerline of the joint and the location is out of the field of view of the SEM-BSE micrograph.

Figure 4.21: X-ray diffraction patterns for the 1150 °C / 70 minute specimen at (a) 800 μm away from the centerline of the joint, (b) 60 μm away from the centerline of the joint near the diffusion zone, and (c) 10 μm away from the centerline of the joint.

4.4 Effect of Bonding Cycle on Parent Material Microstructure

Given the meta-stable nature of the parent material in the SCHAT condition, the high bonding temperature, and a significant isothermal holding time, an expectation exists that the parent material away from the braze zone will potentially exhibit equiaxed spheroidization in microstructure during the bonding cycle [47]. Existing literature for beta solidified TiAl alloys indicate a phase transformation process whereby the metastable fully lamellar α_2/γ microstructure decomposes towards an equiaxed $\alpha_2 + \gamma + \beta_0$ microstructure through the transformation pathway $\alpha_2 + \gamma \rightarrow \alpha_2 + \gamma + \beta_0$ when re-heated during a typical stabilization treatment [29]. During this transformation, the α_2 phase volume fraction within the α_2/γ lamellar colonies contains a high departure from equilibrium. Thus, the α_2 phase reduces in volume fraction towards equilibrium and precipitates an interfacial $\beta_{0,sec}$ phase during the dissolution of α_2 laths resulting in increased $\gamma + \beta_0$. Additionally, the G2 beta gamma alloy utilized in this study does not contain a single α phase field during slow cooling from the SCHAT hold temperature to the $T_{F/A}$ temperature resulting in retained β_0 phase at the colony boundaries when quickly cooled to room temperature. During an additional low temperature stabilization treatment, the intercolony β_0 region will transform either by direct nucleation of the γ phase within the existing retained β_0 phase [27, 35], or through discontinuous coarsening of existing γ laths from the lamellar colony into the intercolony β_0 region towards an equiaxed $\gamma + \beta_0$ microstructure [27].

Table 4.5 and Figure 4.22 indicate the microstructural features associated with the parent material 800 μm away from the bondline. For all three isothermal bonding temperatures, the parent material exhibits a near fully lamellar microstructure with an average colony size ranging from 58-71 μm depending on the bonding temperature, a volume fraction of lamellar colonies of 85-87 vol.%, with intercolony regions primarily composed of the γ phase interspersed with the β_0 phase near colony boundaries (Figure 4.22 a,c,e). Due to the relatively continuous seam-like morphology of the intercolony γ phase that has increased in width and hence volume fraction from the initial 1 vol.% for the SCHAT condition, the intercolony γ phase growth is likely caused by a coarsening mechanism whereby the adjacent lamellar colonies are consumed by

the existing intercolony γ phase through the $\alpha_2 \rightarrow \gamma$ transformation. Such a consumption may partially explain the smaller mean colony size for the 1150 °C bonding temperature. Additionally, the β_0 phase within the intercolony region eventually begins to coarsen due to the $\alpha_2 \rightarrow \beta$ transformation which is known to start after the $\alpha_2 \rightarrow \gamma$ transformation in beta containing ternary gamma alloys at the isothermal holding temperature [35].

In addition to intercolony morphological changes, four additional microstructural features are evident within the colonies themselves depending on the bonding temperature. First, a portion of colonies exhibit significant lamellar coarsening with lamellar size and spacings on the order of microns as is evident by the colonies marked in Figure 4.22a,c,e. The lamellar coarsening results from a decomposition reaction according to $\alpha_2 \rightarrow \beta + \gamma$ resulting in increased thickness of the γ laths, dissolution of the α_2 laths, and the precipitation of secondary $\beta_{0,sec}$ precipitates [28]. The 1090 °C condition appears to exhibit a greater quantity of coarse α_2/γ colonies compared with the 1030 °C condition as the fraction of lamellar colonies for the 1090 °C / 30 minute condition are composed of 29 vol% coarse α_2/γ colonies, while the 1030 °C / 30 minute condition is composed of 5.5 vol.% α_2/γ coarse colonies respectively. The 1150 °C condition exhibits coarse lamellar colonies on the order of the 1090 °C condition as the fraction of lamellar colonies for the 1150 °C / 30 minute condition is composed of 16 vol% coarse α_2/γ colonies. The increase in coarse lamellae colonies has been observed to increase with aging temperature for similar beta stabilized TiAl alloys [23].

Secondly, within the remaining lamellar colonies, the relatively fine lamellar structure is maintained, however the same decomposition reaction causes $\beta_{0,sec}$ precipitation at the expense of α_2 lath dissolution (Figure 4.22b,d,f). With increasing bonding temperature from 1030 °C to 1150 °C, the $\beta_{0,sec}$ precipitates continue to coarsen and lamellar spacings appear to increase. Additionally, for the 1150 °C condition, coarse lamellar colonies exhibit greater growth of the interfacial $\beta_{0,sec}$ precipitate phase with length scales on the order of the intercolony β_0 phase.

Thirdly, sparsely dispersed particles throughout the colonies and colony boundaries are bright blocky precipitates with a size on the order of a few lamellar spacings for 1030 °C and 1090 °C bonding temperatures, which further coarsen to tens of lamellar spacings for the 1150 °C bonding temperature (yellow arrows in Figure 4.22a) . These bright precipitates are likely titanium borides of TiB_2 or TiB constitution as a result of the boron content within the alloy.

Fourth, a globular γ phase within the α_2/γ colonies is evident for the 1090 °C and 1150 °C bonding temperature (dark arrows in Figure 4.22c). This globular γ phase has been observed in Ti-46Al-6(Nb,Mo)-0.2B (at.%) alloys taken through a stabilizing heat treatment at 1100 °C for 2 hours and is attributed to the supersaturation of Nb and Mo elements within the α_2 lamellae that promote the $\alpha_2 \rightarrow \beta + \gamma$ transformation [23, 124].

Table 4.5: Summary of Parent Material Microstructural Features caused by the Diffusion Brazing Bonding Cycle

Test	Mean α_2/γ -Colony	α_2/γ -Colony	Coarse	$\beta_{0,sec}$	Intracolony	Intracolony
No.	Size (μm)	vol. (%)	α_2/γ -Colonies (vol. %)	Precipitation	Borides	Globular γ_{glob}
DB1 (1030/30)	71	86	5.5	+	+	-
DB4 (1090/30)	71	87	29	+	+	+
DB7 (1150/30)	58	85	16	+	+	+

Figure 4.22: SEM-BSE images for 1030 °C/30 min. (a,b), 1090 °C/30 min. (c,d), and 1150 °C/30 min. (e,f) showing the impact of the bonding cycle at various isothermal holding temperatures on the parent material microstructure.

4.5 Kinetics and Morphological Evolution during Diffusion Brazing Beta Gamma Titanium Aluminide

For TiAl diffusion brazed microstructures, limited information as to the mechanisms that control the growth kinetics of the various regions in the joint has been elucidated. Diffusion-controlled reactions, interfacial-controlled reactions, and supply-controlled reactions have all been observed in TLP joints of other metallic systems containing intermetallic phases [91]. An understanding of the mechanisms that control the evolving microstructure in TLP bonded TiAl joints will allow a refinement of the processing parameters to produce a more desirable microstructure. Therefore, in order to compare growth characteristics of the various TLP microstructures, an empirical power law function (Equation 4.1) is widely utilized to describe the growth of intermetallic phases during isothermal diffusion brazing [125,126].

$$\Delta x = kt^n \quad (4.1)$$

where Δx refers to the mean thickness of the associated layer, k is the growth proportionality factor, and n is the growth exponent. The growth exponent n may be determined by taking the natural logarithm of Equation 4.1 where;

$$\ln(x - x_0) = \ln k + n \ln t \quad (4.2)$$

and performing a linear regression analysis of $\ln(x-x_0)$ versus $\ln(t)$. When $n = 0.5$, growth is considered to be controlled by bulk diffusion, while for $n < 0.5$, growth is associated with grain boundary diffusion and eventually grain coarsening as the growth rate falls below 0.33 [125]. As such, an evaluation of the dependence on time and temperature of the evolution of the resultant microstructure may reveal the growth mechanisms associated with each region in the TLP joint.

Microstructural measurements associated with the growth of various multi-phase regions in the joint are carried out to better understand the kinetics and morphological evolution of the resultant DB/TLP microstructures. The mean thickness of the phases within zone 1 (i.e. the semi-continuous α_2 layer, the semi-scalloped type β -Ti layer, and the residual τ_3 phase) were calculated by dividing the total area for a defined number of grains within the BSE-SEM image by the corresponding lateral

length. In a similar fashion, within zone 2, the various regions are delineated by the number of phases, and the thickness of each region is calculated utilizing the same area calculation as for zone 1. For each isothermal hold temperature, the phase transitions differ, and as such, a schematic of each is indicated in Figure 4.23. For the semi-continuous α_2 phase, some spalling and/or nucleation within the brazing liquid occurred. For microstructures including spalling and/or growth across the centerline of the joint, both sides of the layer areas are summed together and a mean equivalent layer thickness determined for each side of the joint.

The mean thickness of the semi-continuous α_2 layer, the β -Ti scallops, the τ_3 phase, as well as the diffusion zone consisting of an $\alpha_2 + \beta_0$ region and the $\alpha_2 + \beta_0 + \tau_3$ region is determined as a function of holding time for three different isothermal solidification temperatures (Figure 4.24). Table 4.6 lists the regions within the bonded zone that follow a power law growth relationship and their associated growth proportionality factor and growth exponent. Not all regions at all bonding temperatures exhibited exponential growth behaviour. For instances where a power law relationship was not observed, the trend in growth behaviour is indicated if applicable. Experimental values for the semi-continuous α_2 layer were best fitted by $n = 0.483$ ($R^2 = 0.998$) at 1030 °C, $n = 0.312$ ($R^2 = 0.994$) at 1090 °C and $n = 0.218$ ($R^2 = 0.95$) at 1150 °C, indicating that as isothermal solidification temperature increases, greater contribution to grain boundary diffusion and eventually grain coarsening takes place. The grain coarsening may be in part due to the formation of the α phase as opposed to the α_2 phase at 1150 °C which may enhance coarsening of α layer at high isothermal bonding temperatures and lower holding times. Lack of experimental data at isothermal holding times less than 30 minutes and the possibility of liquid extrusion from the joint may play a role in the variability of results.

In general terms, at 1030 °C, the 3 phase $\beta_0 + \alpha_2 + \tau_3$ region in the diffusion zone expanded according to grain boundary assisted diffusion controlled mechanisms due to the low exponential growth factor, while the growth of the semi-continuous α_2 phase in zone 1 reveals volume diffusion as the primary kinetic mechanism. The denuded two phase $\alpha_2 + \beta_0$ region in zone 2 is monotonically decreasing likely at the expense of the expanding τ_3 growth near the parent material / diffusion zone 2 interface. Minimal growth of the semi-continuous α_2 phase and scalloped β_0 phase occurred with minimal reduction in residual liquid over the 30-70 minute isothermal solidification times indicating that these phases likely formed at the early stages

Figure 4.23: Schematic showing how the multiphase microstructure throughout the bondzone for each isothermal hold temperature is transformed to a layered structure for kinetic growth calculations (a) 1030 °C, (b) 1090 °C, (c) 1150 °C.

of TLP growth and remained relatively stable for isothermal holding times ranging from 30-70 minutes. The semi-continuous α_2 phase is fitted to a volume diffusion controlled growth mechanism at 1030 °C while the scalloped β_0 -Ti grain growth is fitted with a growth parameter less than 0.5 implying some contribution to grain boundary controlled growth mechanism which has been found for other intermetallic systems under similar bonding configurations with similar scalloped morphology.

Table 4.6: Growth kinetics associated with phase evolution for the 1030 °C bonding temperature

Zone	Region	Kinetic Relationship	k	n	R ²
1	τ_3	–	–	–	–
1	β_0	Power Law	1.855	0.2223	0.9681
1	α_2	Power Law	0.6844	0.4832	0.9981
2	$\beta_0 + \alpha_2$	Monotonically Decreasing	–	–	–
2	$\beta_0 + \alpha_2 + \tau_3$	Power Law	8.851	0.253	0.9848

At 1090 °C, both the three phase diffusion zone and α_2 phase in zone 1 experience power law type growth behaviour (Table 4.7, Figure 4.25). Both regions exhibit a reduction in their respective growth exponents indicating the effect of higher bonding temperature. As the bonding temperature increases from 1030 °C to 1090 °C, greater evolution of the microstructure occurs leading to greater coarsening in the diffusion zone, and a resultant reduction in growth exponent below 0.3 at identical isothermal solidification time. A reduction in the denuded region within zone 2 occurs likely at the expense of the expanding three phase region within zone 2 as was the case for the 1030 °C condition. The higher bonding temperature of 1090 °C likely enhances the reduction of the denuded region compared with the 1030 °C bonding temperature. Both the 1030 °C and 1090 °C isothermal hold temperatures exhibit similar solid-state growth/coarsening mechanisms with the τ_3 phase increasing in volume fraction within the diffusion zone. Within zone 1, the centerline residual liquid is monotonically decreasing as expected, however the growth of the β_0 phase is quite stagnant. It is unknown as to the reason for this stagnation, however the semi-continuous α_2 layer may act as a diffusion barrier for β_0 phase scalloped growth, or variability

Figure 4.24: (a) Bonding region widths as a function of isothermal holding time for a bonding temperature of 1030 °C. Lines in (a) are best fit of the zones experiencing power law growth behaviour based on linear regression analysis of the data in (b).

in experimental conditions such as extrusion of liquid from the joint, variability in bonding pressure, or variability in foil diameter ratio may be playing a role in the variability of results.

Table 4.7: Growth kinetics associated with phase evolution for the 1090 °C bonding temperature

Zone	Region	Kinetic Relationship	k	n	R ²
1	τ_3	Monotonically Decreasing	—	—	—
1	β_0	Monotonically Decreasing	—	—	—
1	α_2	Power Law	1.711	0.3125	0.9935
2	$\beta_0 + \tau_3$	—	—	—	—
2	$\alpha_2 + \beta_0 + \tau_3$	Power Law	13.58	0.2056	0.9412

At 1150 °C, no residual liquid is present after an isothermal holding time of 30 minutes indicating that the liquid has been completely consumed and a complete liquid to solid phase transformation has occurred across the joint prior to cooling. The centerline β_0 phase is decreasing at the expense of the semi-continuous α_2 phase which is evident both by the layer measurements and by the BSE-SEM micrographs (Figure 4.19). The growth exponent associated with the α_2 phase ($n = 0.219$, $R^2=0.95$) is consistent with grain coarsening (Table 4.8). Within the diffusion zone, the denuded three phase region experiences power law growth with a low growth exponent ($n = 0.2166$, $R^2 = 0.98$) consistent with grain coarsening, while the expanding 4 phase region appears to be experiencing exponential type growth. The variability of layer measurements for the diffusion zone may be due to the significant coarsening at colony boundaries and intercolony regions making discrimination between unaffected parent material and the diffusion zone more difficult.

Figure 4.25: (a) Bonding region widths as a function of isothermal holding time for a bonding temperature of 1090 °C. Lines in (a) are best fit of the zones experiencing power law growth behaviour based on linear regression analysis of the data in (b).

(a)

(b)

Figure 4.26: (a) Bonding region widths as a function of isothermal holding time for a bonding temperature of 1150 °C. Lines in (a) are best fit of the zones experiencing power law growth behaviour based on linear regression analysis of the data in (b).

Table 4.8: Growth kinetics associated with phase evolution for the 1150 °C bonding temperature

Zone	Region	Kinetic Relationship	k	n	R ²
1	$\beta_0 + \gamma + \tau_3(C/L)$	—	—	—	—
1	α_2	Power Law	3.917	0.2185	0.9471
2	$\beta_0 + \gamma + \tau_3$	Power Law	8.408	0.2166	0.9806
2	$\beta_0 + \gamma + \alpha_2 + \tau_3$	Exponential	—	—	—

4.6 Structure-Property Relationships for As-Bonded TiNi Joints: Braze Zone Microhardness

Microhardness measurements were conducted across the bonds for all isothermal holding time and bonding temperature combinations (Figure 4.27). For the 1030 °C and 1090 °C bonding experiments, the hardness within the braze region has significantly increased over the initial parent material microhardness in the SCHAT condition. Peak hardness values ranging from 750-950HV and 625-850HV for the 1030 °C and 1090 °C experiments respectively, while the initial SCHAT hardness within lamellar colonies of the parent material is 480HV. This two-fold increase in hardness is attributed to a number of factors. The primary factor contributing to the high hardness at the bond centerline is the existence of the semi-continuous globular τ_3 ternary intermetallic phase with a maximum volume fraction in the braze zone of approximately 20 vol.% (Figure 4.28). The τ_3 intermetallic phase is a hexagonal polymorph laves phase of the MgZn_2 type (C14) [127]. Laves phases generally exhibit high hardness and brittleness at room temperature due to their complex TCP structure and resistance to dislocation motion. Plastic deformation in laves phases generally occurs above $0.67T_m$ via a synchroshear mechanism [128]. Since this deformation mechanism is difficult at low temperature, laves phases are generally brittle at room temperature. The ternary intermetallic phases within the Ti-Al-Ni system have been found to exhibit hardness levels on the order of 850 HV for brazing experiments conducted on γ -TiAl [96], consistent with the results found for the 1030 °C and 1090 °C diffusion brazing specimens in this study.

The second factor contributing to an overall hardness increase within the braze zone is the high volume fraction (25-80 vol.%) of the β_0 phase present in the microstructure. The β_0 phase is known to be the highest hardness phase at room temperature amongst the α_2 , γ , and β_0 phases for TNM alloys [129]. The third factor contributing to the high hardness in the braze zone is the high volume fraction (15-60 vol.%) of the α_2 phase. The α_2 phase is known to be approximately 3 times stronger than the γ phase for high Nb bearing TiAl alloys [130], and the increase in α_2 volume fraction has been found to be directly proportional to the increase in hardness for fully lamellar TiAl microstructures [131].

For the 1150 °C bonding condition, a decrease in microhardness (580-680HV) occurs over both the 1030 °C and 1090 °C diffusion brazing experiments (680-850 HV). The reduction in microhardness can be attributed to the mutual reduction in volume fraction of the τ_3 and β_0 phases, with an increase in the γ phase (Figure 4.28). The general coarsening of the microstructure within the braze zone for the 1150 °C bonding condition may also contribute to reduced hardness through reduced grain boundary area. However, as the Al content increases within the braze zone, solid solution strengthening effects may offset the reduction in hardness that is achieved via α_2 and τ_3 phase reduction [132]. For diffusion braze experiments conducted at 1090 °C and lower, significant volume fraction of high hardness phases of the τ_3 , β_0 , and α_2 contribute to the high hardness within the braze zone, which is confirmed by the direct correlation associated with microhardness and volume fraction measurements across the braze zone for the 1030 °C/30 minute and 1150 °C/70 minute condition (Figure 4.28).

(a)

(b)

(c)

Figure 4.27: Microhardness measurements across the braze zone for (a) 1030 °C, (b) 1090 °C, and (c) 1150 °C TLP experiments

(a)

(b)

Figure 4.28: Measured volume fraction of various phases across the braze zone for (a) 1030 °C / 30 minute condition, (b) 1150 °C / 70 minutes condition.

4.7 Summary

Microstructural and mechanical property evaluation has been conducted for diffusion brazing experiments of a TiAl-2Nb-2Mo beta-gamma alloy bonded with a commercial TiNi67 foil interlayer. Isothermal temperature ranged from 1030 °C to 1150 °C and isothermal solidification times were conducted ranging from 30 minutes to 70 minutes. The following results were found;

1. For diffusion brazing experiments conducted at 1030 °C and 1090 °C, a semi-continuous α_2 structure formed at the solid/liquid interface producing two distinct zones within the braze zone. The central zone consisted of a two phase mixture of β_0 -Ti and a ternary intermetallic phase found to be τ_3 rich in nickel with high hardness as a result of residual liquid cooling. The diffusion zone consisted primarily of $\beta + \alpha_2$ phases with orientation influenced by the lamellar substrate. A nickel rich τ_3 phase was also present in the diffusion zone with a globular or acicular morphology depending on the bonding time and temperature.
2. No γ phase was found within the braze zone for diffusion brazing experiments conducted at 1030 °C. A small quantity of γ phase was found for diffusion brazing experiments conducted at 1090 °C within the diffusion zone which continued to coarsen with increased holding time at 1090 °C.
3. For diffusion brazing experiments conducted at 1150 °C, a semi-continuous layer of disordered α phase formed at the solid/liquid interface enhancing the isothermal solidification rate compared with experiments conducted at 1030 °C and 1090 °C where the ordered α_2 was proposed to have formed at the solid/liquid interface. The enhanced isothermal solidification rate resulted in complete isothermal solidification prior to reaching an isothermal solidification time of 30 minutes. The central zone consisted of no residual liquid on cooling and a high volume fraction of $\beta + \gamma$ phases throughout the bond microstructure along with a finely dispersed Ni rich τ_3 phase.
4. The parent material away from the bondline exhibited lamellar volume fraction reduction to 85-87 vol.%, an increase in coarse lamellar colonies with increasing bonding temperature, increased $\beta_{0,sec}$ precipitation and growth with increasing

bonding temperature, and the formation of intracolony globular γ phase at the 1090 °C and 1150 °C bonding temperatures.

5. The growth kinetics associated with each phase within the braze zone were fit to a power law relationship where applicable. The semi-continuous α_2 phase present at all three microstructures exhibited increased microstructural evolution with increasing diffusion brazing temperature. Fitting the measured semi-continuous α_2 layer to a power law relationship reveals that volume diffusion plays a significant role at 1030 °C, while grain boundary diffusion contributed to growth of the α_2 layer at 1090 °C, and eventually grain coarsening became the dominant kinetic mechanism at 1150 °C.
6. Microhardness measurements revealed a marginal decrease in hardness as isothermal holding times increased due to homogenization of the braze zone microstructure. With increased isothermal solidification temperature, hardness levels decreased from a peak of 850 HV for low temperature bonds, to 580 HV for the 1150 °C/70 minute diffusion brazing specimens. The decrease in microhardness at the 1150 °C bonding temperature is attributed to the reduction in volume fraction of Ni rich τ_3 phase as the centerline of the bond, in addition to increased γ phase volume fraction throughout the braze zone.

Chapter 5

Characterization of Post Bond Heat Treated TiNi Joints

5.1 Post Bond Heat Treatment Design

In order to produce an optimized bond for creep resistance utilizing TiNi-67 foil, post bond heat treatments (PBHT) are required to alter the as-bonded microstructure. The as-bonded microstructure contains a number of detrimental features including; (1) the loss of a fully lamellar well-interlocked microstructure, (2) reduced lamellar volume fraction away from the bond zone, (3) coarsening of lamellar spacings within α_2/γ colonies away from the bond zone, (4) significant volume fraction of the brittle τ_3 ternary intermetallic phase within the bond zone, and (5) centerline porosity. Thus, a post bond heat treatment designed to re-generate the fine fully lamellar microstructure across the bond zone and within the prior parent material is required to maintain the creep performance of the overall TLP structure.

5.1.1 Laves Phase (τ_3) Elimination through Homogenization

In the Ti-Al-Ni ternary system, the τ_3 phase is known to be stable within a temperature range of 750 °C to 1289 °C upon which the Ni-rich τ_3 phase melts congruently according to a reaction where $L = \beta Ti + \tau_3$ [121]. Within the braze zone at 1150 °C, a large 2-phase $\beta_0 + \tau_3$ region is observed. Since this 2-phase field region is potentially stable up to 1289 °C, it may be difficult to remove the τ_3 phase with a homogenization temperature below 1289 °C unless the Ni composition within the 2-phase field region is reduced to within the solubility limits of the β -Ti phase at the homogenization

temperature for which the τ_3 phase is generally embedded. Since a liquid transformation potentially occurs above 1289 °C for the 2-phase field region, the probability of voiding or porosity within the braze zone is increased. The likelihood of voiding or porosity will depend on the heat-up rate to the homogenization temperature and any associated composition changes or phase transformations. During the heat-up stage of the PBHT, the compositional relaxation that occurs may alter the 2-phase field regions in the braze zone such that the nominal congruent composition at 1289 °C does not occur and hence avoidance of the liquid transformation is achieved. The nominal Ni content associated with the 2-phase field is less than 5 at.% Ni, and the congruent transformation occurs at a nominal Ni composition of approximately 12 at.%Ni [121]. Below this Ni composition level, a Ni rich single β phase field occurs according to the liquidus projection. Therefore, as long as additional partitioning or segregation of Ni does not occur towards the 2-phase field region, it should be possible to increase the temperature above 1289 °C and avoid a liquid transformation during homogenization.

5.1.2 Al lean TiAl and the Ability to Re-Form a Fully Lamellar Microstructure

A fully lamellar microstructure is achievable with Al lean binary compositions down to approximately 38 at.%Al [133,134]. The fully lamellar microstructure is achieved via the $\alpha \rightarrow \alpha_2 \rightarrow \alpha_2 + \gamma$ transformation for Al lean binary TiAl alloys as opposed to the more common $\alpha \rightarrow \alpha_2 + \gamma$ transformation typified for TiAl alloys with rich Al compositions (between 40-48 at.% Al). For typical beta-gamma alloys, the transformation pathway includes the β phase, as the addition of group V and VI transition elements stabilizes the β phase to lower temperature and higher Al content. However, due to the detrimental aspects of the β phase during high temperature service, nominal compositions are generally tailored to minimize the β phase volume fraction on cooling in order to form a fine fully lamellar creep resistant microstructure. A typical transformation pathway includes the generation of α grains and small quantities of the β phase which typically form at α grain boundaries and assist in retarding α grain growth during heat treatment [35]. On quick cooling, the α phase present at the heat treatment temperature will transform via the $\alpha \rightarrow \alpha_2 + \gamma$ lamellar transformation, while the remaining β phase will undergo a $\beta \rightarrow \beta + \gamma$ transformation. It is possible to fully suppress the β phase in beta-gamma alloys if equilibrium is achieved in the single

α phase field prior to cooling, however, excessive α grain growth may occur depending on the holding time, resulting in a coarse fully lamellar microstructure [129].

In order to maximize the lamellar volume fraction for in-service operation, the β phase must be minimized at the transition from furnace cooling to air cooling during the SHT. The typical transformation pathway for beta gamma alloys relies on the minimization of the beta phase through slow (near equilibrium) cooling from a region high in the $\alpha + \beta$ phase field to just above the α transus temperature in order to maximize the α phase prior to cooling. Typically, alloy compositions are tailored to produce such a microstructure, however, the microstructure is sensitive to changes in constitution. For TNM alloys, it was found that combined variations in Nb/Mo content on the order of 1 at.% Nb, and 0.5 at.% Mo results in an increase in the β phase minimum volume fraction from approximately 8 vol.% to 18 vol.% at the alpha transus temperature based on ex-situ methods [29]. Given the sensitivity of the resultant phase fractions within the parent material to both beta stabilizing element content, and the $T_{F/A}$ temperature [40], minimizing the β phase in the center of the joint without altering the composition will likely be difficult.

With a depleted Al region in the braze zone on the order of 38-42 at.%Al for the TiNi-67 as-bonded specimens, the ability to maximize the α phase and minimize the β phase within the $\alpha + \beta$ phase field is hampered by the contracting $\alpha + \beta$ phase field, and lower $T_{\beta \rightarrow \alpha + \beta}$ transition temperature that occurs with decreasing Al content (Figure 5.1). For significantly Al lean alloys less than or equal to 42 at.%Al, the β phase volume fraction may in fact remain at 100 vol.% β depending on the $T_{F/A}$ temperature and quantity of beta stabilizing elements within the braze zone, resulting in retained β phase on cooling (shaded region in Figure 5.1). Additionally, even for compositions with intermediate beta forming effectiveness and an optimized $T_{F/A}$ temperature that maximizes the $\alpha + \beta$ phase field, the equilibrium $\alpha + \beta$ phase fraction on cooling may remain high.

At the other end of the spectrum, where the composition is lean in both Al content and beta stabilizing elements, avoidance of the $\alpha + \beta$ phase field at the $T_{F/A}$ temperature is also possible (shaded region in Figure 5.2). Under such conditions, the β phase will also likely be retained on quick cooling from the $T_{F/A}$ with a typical transformation pathway according to $\beta \rightarrow \alpha_2 + \beta_0 \rightarrow \alpha_2 + \beta_0 + \gamma$. Therefore, optimization of the homogenization temperature and $T_{F/A}$ temperature is likely required to maximize the lamellar volume fraction within the braze zone. However,

Figure 5.1: Ti-(42-44)Al-xMo at.% phase diagrams indicating the contraction of the $\alpha + \beta$ phase field with decreasing Al content from 44 at.% Al to 42 at.% Al for ternary Ti-Al-Mo compositions. The shaded region in the Ti-42Al-xMo at.% phase diagram indicates a range of Mo content that completely avoids the two phase $\alpha + \beta$ region.

the G2 parent material exhibits particular sensitivity to the $T_{F/A}$ temperature which may detrimentally alter the parent material microstructure if the $T_{F/A}$ temperature is not maintained to within an optimum 1275-1285 °C temperature range [40]. An ideal balance between detrimentally affecting the parent material, and maximizing the lamellar volume fraction within the braze zone is required.

With the additional complication of adding Ni to the parent material, a method is required to evaluate the additional effect of Ni on the beta forming effectiveness of the composition within the braze zone. The beta forming effectiveness equivalency utilizing Mo, Nb, and Ni is proposed in this work based on the equivalency definition proposed by Kobayashi et al. [34] for quaternary compositions, but extended in this work to a pentanary system. Starting with a quaternary system composed of Ti-Al- M_1 - M_2 where M_1 and M_2 are beta stabilizing elements, the M_1 equivalency of M_2 is found by relating the M composition at which the three phase tie-triangle phase boundary is crossed for constant temperature and constant Al content. The coefficient

$$k_{M_1/M_2} = X_{M_1}/X_{M_2} \quad (5.1)$$

Figure 5.3: Beta forming effectiveness of Nb and Ni compared against Mo for various Al compositions at 1200 °C.

Figure 5.3 is the 2x greater β stabilizing effect that Ni imparts across typical Al concentrations compared with Mo, as well as the relatively low beta forming effectiveness of Nb compared with Mo.

Utilizing Figure 5.3, the effective Mo equivalent of the as-bonded 1150 °C / 70 minute microstructure is calculated based on EDS line scans. Figure 5.4 shows that the Mo^{eq} content within the bond zone reaches a maximum value of 12 at.% (Mo^{eq}), with typical values of 6-8 at.% Mo^{eq} within $\pm 100 \mu m$ of the centerline of the bond. Additionally, as the Al content decreases from the nominal value of the parent material, a proportional increase in the beta forming effectiveness of the braze zone is observed (Figure 5.5).

The Mo^{eq} statistical data (standard deviation and range) associated with the 42, 43, and 44 at.% Al compositions for the 1150 °C / 70 minute condition within the braze zone are plotted on the Ti-(42-44)Al-xMo phase diagrams shown in Figure 5.6. Without further homogenization of the bond zone, a high volume fraction of the β phase at a $T_{F/A}$ temperature of 1280 °C is likely, and when the Mo^{eq} composition is

Figure 5.4: Mo^{eq} equivalency calculation for the 1150 °C / 70 min. condition across the bond zone based on EDS measurements (Ti removed for clarity).

Figure 5.5: Mo^{eq} versus Al content for the 1150 °C / 70 min. condition across the bond zone based on line scan EDS measurements.

greater than Ti-42Al-5.3Mo^{eq}, a single β or $\beta + \gamma$ phase field occurs at all temperatures. On rapid cooling, regions containing Ti-42Al-(5.3-8)Mo^{eq} at.% in the single β phase region will likely be retained to room temperature. Therefore, to achieve a homogenized fully lamellar region across the bond zone, the following methodology is proposed:

1. To promote homogenization across the bond zone prior to reaching the congruent melting temperature of the τ_3 phase of 1289 °C, a reduced heating rate of 20 K/min is implemented for all solutionizing heat treatments.
2. A solutionizing temperature of 1400 °C for 40 minutes is utilized to homogenize the microstructure based on prior studies on the parent material that resulted in an attractive fine fully lamellar microstructure from the HIP'd condition [40].
3. As the aluminum content reduces from 44 at.% to 42 at.%, the equilibrium volume fraction of the β phase at the $T_{F/A}$ temperature of 1280 °C based on a lever rule approach reduces from approximately 70 vol.% to 50 vol.% (Figure 5.6). Therefore, an Al content across the bond zone greater than 42 at.% is required to minimize the equilibrium volume fraction of the β phase at the $T_{F/A}$ temperature by ensuring a large $\alpha + \beta$ phase region encompassing as large an Mo^{eq} composition as possible prior to quick cooling. The high solutionizing temperature and time is envisioned to promote this aluminum homogenization.
4. A reduction of the Mo^{eq} composition to within +/- 0.5 at.% of the nominal Mo^{eq} value of the parent material is required in order to minimize the volume fraction of the β phase prior to cooling from the $T_{F/A}$ temperature of 1280 °C. The high solutionizing temperature and time is envisioned to promote this reduction in Mo^{eq} composition across the bond zone.
5. The $T_{F/A}$ temperature of 1280 °C is selected based on prior studies that revealed the sensitivity of the parent material to a variation of +/- 10 °C in $T_{F/A}$ temperature deviation that detrimentally affected the parent material microstructure [40].

Figure 5.6: Ti-(42-44)Al-xMo at.% phase diagrams indicating the standard deviation (blue shaded region) and range (red shaded region) of Mo^{eq} compositions found within the braze zone for the 1150 °C / 70 min. condition from 44 at.% Al to 42 at.% Al.

5.2 Post Bond Heat Treated SCHT Microstructure Evaluation

Selected as-bonded specimens (1150 °C / 70 minutes) were subjected to a post bond step-cooled solutionizing heat treatment (PB-SCHT1, Table 3.4) identical to that of the parent material prior to bonding (i.e. 1400 °C / 40 minutes $\rightarrow$ 1280 °C at 12 °C/min $\rightarrow$ AC). The goal of the PB-SCHT is to transform the multi-phase globular type morphology within the bond zone to that of a fine fully lamellar (FL) microstructure, and to ensure that the parent material is re-transformed to the ideal fully lamellar microstructure associated with the optimized SCHT condition prior to bonding.

PB-SCHT microstructures within $\pm$ 400 μ m of the centerline of the bond (Figure 5.7) consist of lamellar colonies surrounded by a dual-phase intercolony region along with evidence of minor spherical and elongated porosity. Within the lamellar colonies, intracolony dual-phase regions are also evident (Figure 5.8). EDS point analysis (Table 5.1, Figure 5.8) reveals that the α_2/γ lamellar colonies at the centerline of the bond contain slightly higher than nominal aluminum content of 45.7 at.% Al, an Nb/Mo content depleted by approximately 0.8 at.%, and an increase in

nickel content to 0.5 at.% Ni. The intercolony regions contain a dark phase found at both the lamellar colony interfaces, as well as embedded within the bright intercolony phase at colony boundary triple points. Both dark phases have a composition consistent with the γ -TiAl phase. The light intercolony phase is significantly lean in aluminum content (38 at.%Al), and contains higher than nominal levels of Mo (3 at.%Mo), with significant Nb and Ni concentrations greater than 1.5 at.% respectively. It is postulated that the light intercolony phase is the β_0 phase due to the high concentration of β -stabilizing elements, and specifically the high concentration of Mo which is known to have a greater partition ratio compared with Nb for similar β -solidifying alloys [19]. No evidence of a fourth phase is apparent in the SEM-BSE micrographs indicating that the τ_3 phase present in the as-bonded condition has been eliminated via the PB-SCHT. Furthermore, EDS line scans (Figure 5.9) taken across the bond zone confirm the Al-lean intercolony regions, and the Mo "spikes" that correspond with the existence of the intercolony $\beta_0 + \gamma$ mixture (Figure 5.9a and Figure 5.9b). In addition to the Mo segregation within the β_0 phase, a slight nickel gradient exists from the centerline of the bond zone towards the parent material with a maximum nickel content of 1.5-2.0 at.% Ni which decreases to less than 0.5 at.% Ni at an approximate distance of 600 μm from the centerline of the bond. Additionally, a slight aluminum concentration gradient is evident characterized by a slight upswing in the Al concentration at a distance of 600 μm from the centerline of the bond. The upswing in the Al concentration curve indicates that the Al content remains slightly depleted within the braze zone compared with the parent material substrate.

Table 5.1: Summary of EDS spot analysis on the 1150 °C / 70 min. + PB-SCHT condition near the centerline of the braze zone

Zone	Phase	Ti	Al	Nb	Mo	Ni	Ti/Al	Possible
No.	No.	(at%)	(at%)	(at%)	(at%)	(at%)	Ratio	Phases
1	A	55.9	38.0	1.6	3.0	1.5	1.47	β_0
	B	48.6	48.4	1.4	1.1	0.5	1.00	γ
	C	51.4	45.7	1.3	1.1	0.5	1.12	α_2/γ

An intercolony network of β_0 phase interspersed within lamellar colonies typically forms when titanium aluminides are solidified through the single β phase field [30]. As the specimen is heated to the solutionizing temperature, a seam of the β phase forms around α grains and assist in inhibiting α grain growth. The intracolony β_0 phase forms due to the rejection of beta stabilizing elements into the α/β interphase during the $\beta \rightarrow \alpha$ phase transformation [30]. Both the cooling rate and dwell time at the PB-SCHT temperature affect the inter and intra colony formation of the β_0 phase as well as the formation of the intercolony γ phase. With increased dwell time in the single β phase field, the β phase seam continues to expand at the expense of the α grains towards equilibrium. On cooling from the PB-SCHT temperature, upon crossing the γ solvus, the γ phase nucleates at the α/β interphase and consumes the α phase until such time that the remaining α phase undergoes a transformation to an α_2/γ lamellar colony.

As distance increases from the centerline of the bond, a decrease of both intercolony and intracolony $\beta_0 + \gamma$ phases occurs (Figure 5.10) suggesting that the bond zone contains higher than nominal beta forming elements which is confirmed through EDS line scans (Figure 5.9). Volume fraction measurements of lamellar colonies indicate a minimum lamellar colony volume fraction on the order of 75 vol.% that occurs within $\pm 150 \mu\text{m}$ of the centerline of the joint that sharply increases to volume fractions on the order of 90 vol.% between $\pm 150\text{-}400 \mu\text{m}$ from the centerline of the bond. As such, this region of the bond zone is considered to be a “near-lamellar β ” microstructure. The morphology of the lamellar colony interfaces within this region are not well interlocked due to the seam of intercolony $\beta_0 + \gamma$ phases surrounding the α_2/γ -colonies that is approximately $9\text{-}12 \mu\text{m}$ wide. Lamellar colony size measurements (Figure 5.11) reveal a mean lamellar colony size at the centerline of the bond of $64 \mu\text{m}$, with slight colony elongation perpendicular to the bondline.

Greater than $\pm 400 \mu\text{m}$ from the centerline of the joint, the volume fraction of lamellar colonies increases to greater than 98 vol.% and is considered a “fully lamellar” microstructure with an apparent increase in the degree of interlocked colonies increasing as the distance from the centerline increases which is evident by the reduction in intercolony seam width (Table 5.2). As the distance increases from the bondline, the colonies become more equiaxed in nature, with a slight increase in mean

colony size to approximately 90 μm .

Coarse lamellar colonies with lamellar spacings on the order of microns are evident at the centerline of the bond with a volume fraction of 8.5 vol.%. The volume fraction of coarse lamellar colonies decreases with increasing distance from the centerline to less than 2.0 vol.% at 1000 μm from the centerline of the bond (Table 5.2). In the as-bonded condition, the parent material away from the bond zone contained coarse lamellar colonies on the order of 13 vol.%. Therefore, the PB-SCHT treatment is successful in reducing the quantity of coarse lamellar colonies within the parent material, while the degree of coarse colonies within the braze zone is similar to that of the parent material in the as-bonded condition. High magnification images of the fine lath structure within the bond zone and 800 μm away from the bond zone reveal no evidence of secondary $\beta_{0,sec}$ phase precipitation (Figure 5.12).

Due to the constitution of the braze zone, the PB-SCHT hold temperature is possibly within the single β phase field. As such, significant chemical homogenization of the braze zone is possible due to fast diffusing species that occurs in the disordered β phase at this temperature. Depending on the degree of homogenization in the braze zone, and the T_β transition temperature, the slow-cooling step to the $T_{F/A}$ temperature of 1280 $^\circ\text{C}$ from 1400 $^\circ\text{C}$ will likely transform part of the braze zone to the α phase producing a dual-phase $\alpha + \beta$ mixture. Since the microstructure at the centerline of the braze zone contains 75 vol.% lamellar colonies, the intercolony region composed of $\beta_0 + \gamma$ is a result of a $\beta \rightarrow \beta + \gamma$ transformation for compositions that contain greater than nominal beta forming effectiveness.

Swaighoffer et al. [28] has found that a fine fully lamellar microstructure with greater than 97 vol.% lamellar colonies is possible in the TNM alloy when air cooled from a solutionizing temperature in the single β phase field. Air cooling from the β phase field will produce a fully lamellar structure when the composition of the alloy exhibits the $\alpha_2 + \beta_0 + \gamma$ phase field below the eutectoid temperature. The extent of the three phase field is dependent on both the Al content and the beta stabilizing elements. In this work, the PB-SCHT was not air cooled, but the elements in the furnace were turned off and flowing argon was back-filled into the hot zone of the furnace chamber producing a cooling rate on the order of 70-90 $^\circ\text{C}/\text{min}$ from the $T_{F/A}$ temperature to below the eutectoid temperature. In this instance, a high volume fraction of lamellar colonies was still achievable in both the bond zone and the parent material away from the bond zone.

Compared with the parent material condition prior to bonding, the PB-SCHT was successful at producing a fine fully lamellar microstructure in the parent material, while the braze zone region contains a slightly higher volume fraction of coarse colonies, and reduced volume fraction of lamellar colonies. Beneficial aspects of the PB-SCHT include:

1. An increase in lamellar volume fraction from 0 vol.% in the as-bonded condition to 75 vol.% in the PB-SCHT condition at the centerline of the joint.
2. Apparent elimination of the τ_3 laves phase from the bond zone.
3. A mean colony size at the centerline of the joint of 64 μm which is on the order of the parent material colony size prior to brazing.
4. Fine and continuous lamellar size and spacing in the sub-micron range for colonies within the bond zone and within the parent material.
5. Well interlocked fully lamellar colonies away from the bond zone with little to no intercolony $\beta_0 + \gamma$ growth.
6. The elimination of globular γ phases within the parent material microstructure that manifested as a result of the diffusion brazing cycle.

Challenges remain within the PB-SCHT microstructure including:

1. Although the volume fraction of lamellar colonies is high within the bond zone, a fully lamellar structure is not achieved, and the continuous intercolony regions of approximately 9-12 μm will likely cause a reduction in creep resistance.
2. The degree of coarse lamellar colonies may also impact the creep response to to the reduced ability to hinder dislocation emission and motion.
3. The existence of porosity may also lead to premature void coalescence impacting the creep response.
4. The unknown impact of elevated Ni content on the stability of the intercolony $\beta_0 + \gamma$ region and lamellar structure within the bond zone.

(a)

(b)

Figure 5.7: Bonded specimen (1150 °C / 70 min.) subjected to a step cooled solutionizing heat treatment of 1400 °C for 40 minutes → 11 °C/min to 1280 °C → AC. (a) Heat tinted brightfield optical micrograph at 100x magnification (b) SEM-BSE micrograph at 200x magnification

Figure 5.8: SEM-BSE images of the 1150 °C / 70 min. bonded sample subjected to a step cooled solutionizing heat treatment near the centerline of the joint (5000x magnification)

Figure 5.9: EDS line scan plots of the 1150 °C / 70 min. bonded sample subjected to a step cooled solutionizing heat treatment (a) Ti and Al compositions, (b) Nb, Mo, and Ni compositions

Figure 5.10: Lamellar colony volume fraction versus distance from centerline for the 1150 °C / 70 min. + PB-SCHT condition

Figure 5.11: (a) Heat tinted optical micrograph showing the bond zone (100x) and location of colony size measurements., (b) histogram of colony size measurements at the associated distances from the centerline of the bond. Vertical dashed lines within each histogram indicate mean colony size

Figure 5.12: SEM-BSE micrographs of the lamellar structure for the 1150 $^{\circ}\text{C}$ / 70 minute condition subjected to a PB-SCHT (a) lamellar structure within the bond zone colonies, (b) lamellar structure in the parent material colonies.

Table 5.2: Summary of microstructural features associated with various locations from the centerline of the 1150 °C / 70 min. + PB-SCHT bond

Distance from Centerline (μm)	Type of Microstructure	α_2/γ -colony				Mean Intercolony Seam Width (μm)
		Fraction (vol.%)	Mean Diameter (μm)	Coarse Fraction (vol.%)	Fine Fraction (vol.%)	
0	NL- β	87	64	8.5	78.5	9.9
100	NL- β	93	82	7.7	85.3	12.1
275	NL- β	98	79	8.2	89.8	5.3
450	FL	99	88	7.8	91.2	3.4
600	FL	99	82	5.4	93.6	2.4
800	FL	99	90	2.0	97.0	1.6
1000	FL	99	87	1.9	97.1	1.5

5.3 PB-SCHT + Aged Microstructure Evaluation

For un-bonded SCHT G2 parent material that has been aged at 900 °C for 6-96 hours, secondary reactions are typical within the microstructure [40]. These reactions include the precipitation of an interfacial $\beta_{0,sec}$ precipitate phase at the lamellar interfaces as well as the growth of intercolony $\gamma + \beta_0$ at the α_2/γ colony boundaries consistent with a cellular reaction. Bonded (1150 °C / 70 minute) + PB-SCHT samples were further subjected to an aging heat treatment at 900 °C for 6 and 24 hours in an attempt to stabilize the microstructure and precipitate interfacial beta phase precipitates ($\beta_{0,sec}$) within both the unaffected parent material lamellar colonies and the braze zone lamellar colonies.

PB-SCHT and aged microstructures within +/- 300 μm from the centerline of the bond consist of lamellar colonies surrounded by, at minimum, a tri-phase intercolony region (Figure 5.13). The volume fraction of lamellar colonies within the bond zone remains relatively stable when compared with the PB-SCHT microstructure. A slight decrease in minimum lamellar volume fraction is observed to 70 vol.% and 72 vol.% for the 6 hour and 24 hour aged condition respectively (Figure 5.14) likely due to a similar coarsening mechanism as a result of the metastable condition associated with the intermediate cooling rate from the $T_{F/A}$ temperature. However, within the very centerline of the bond, the volume fraction of fully lamellar colonies increases to 85 vol.% and 93 vol.% for the 6 hour and 24 hour condition respectively.

As a result of the aging treatment, the intercolony region in addition to slight coarsening within the bond zone, contain the existence of two secondary precipitates embedded within the intercolony β_0 phase. As indicated in section 5.2, the intercolony region of the as-bonded+PB-SCHT condition contains only the globular $\beta_0 + \gamma$ phases. When subjected to an isothermal aging treatment at 900 °C for 6 hours, the intercolony β_0 phase decomposes to manifest an additional high aspect ratio dark platelet phase (Phase C in Figure 5.15a), and a bright globular phase (Phase D in Figure 5.15a). Both 6 hr and 24 hr aged samples exhibit the existence of these secondary precipitates (Figure 5.15b).

EDS spot analysis conducted on the phases within the intercolony region (Table 5.3) reveal the large dark globular phase (B) found at both the lamellar colony interfaces and within the intercolony β_0 phase has a composition consistent with

the γ -TiAl phase. The smaller high aspect ratio platelet dark phase (C) embedded within the intercolony β_0 phase contains a slightly higher quantity of titanium (approx. 57-58 at.%Ti) and lower aluminum content (approx. 36-37 at.%Al) with near nominal Nb and Mo beta forming elements with a Ni content of 2 at.%. Given the fine nature of the dark platelet precipitates, it is somewhat difficult to ascertain the composition and hence potential phase identification from EDS spot analysis. Based on composition alone, the Ti/Al ratio and beta forming elements are consistent with a β_0 phase. Prior studies have found that for ternary titanium aluminide alloys with similar transition elements, Ti/Al ratios for β_0 phase particles fall between 1.48-1.68 with β forming elements on the order of 4-12 at.% [135]. Based on compositional contrast in the BSE-SEM imaging, the dark platelet phase has a similar appearance as the globular intercolony γ phase, and is a plausible phase due to the typical decomposition of $\beta_0 \rightarrow \beta + \gamma$ that is known to form on aging the parent material alloy. However the EDS compositional results for typical γ phases for both the G2 parent material and within the literature invariably reveal a Ti/Al ratio between 1.1-1.3, and such a ratio was not measured for the dark platelet phase. Additionally, based on the equilibrium Ti-Al-Ni phase diagram at 900 °C, the possibility exists that the dark platelet phase is the α_2 phase. The solubility limit of nickel within the α_2 phase is approximately 2 at.% Ni on the 900 °C ternary phase diagram, which corresponds well with the measured nickel composition based on EDS spot analysis. Additionally, the Ti/Al ratio of this platelet phase is high and near the titanium rich end of the single α_2 phase field. One caveat associated with the decomposition of the β_0 phase towards an α_2 phase is that such a decomposition is generally hindered due to the HCP type crystal structure of the α phase as was found for conventional titanium alloys [136]. However, such a transformation has been found to occur for titanium alloys containing similar transition elements (i.e. Fe) where the transition element is found to decompose from the β_0 matrix according to a reaction whereby $\beta \rightarrow \text{TiFe} + \alpha_2$ [137]. As will be explained in the following paragraph, beta phase splitting may be a further potential mechanism associated with the formation of the two unidentified secondary precipitates within the intercolony β_0 phase.

EDS spot analysis conducted on the light spherical phase embedded within the intercolony β_0 phase reveals a nickel content on the order of 7 at.%Ni with Mo content on the order of 3 at.%Mo, Nb content on the order of 2 at.%Nb, and aluminum content on the order of 38 at.%Al. Based on EDS spot analysis, it is suggested

that the light spherical phase may possibly be a result of beta phase splitting as opposed to τ_3 precipitate formation. In conventional beta titanium alloys, solute rich metastable beta phase regions may decompose on aging via $\beta \rightarrow \beta_r + \beta_l$ where β_r is a solute rich region and β_l is a solute lean region [136]. The solute lean region is designated β' and generally exists as coherent BCC zones within the beta rich matrix. Beta phase splitting is known to occur in alloys with a beta phase composition that precludes the formation of an omega phase. In beta gamma alloys of significant beta forming effectiveness, evidence of the decomposition of the β_0 phase to that of an ω_0 or ω'' phase have been known to occur during stabilization treatments at intermediate temperatures [49]. The partitioning behaviour during growth of the ω_0 phase indicates that increased Mo content leads to stabilization of the β_0 phase as opposed to the ω_0 phase [49]. The G2 alloy utilized in this work inherently suppresses ω_0 phase formation to lower temperatures due to the balance between nominal Nb and Mo constituents. The low (7 at.%) Ni content measured through EDS of the bright globular phase compared with that of an equilibrium τ_3 phase (i.e. 20 at.% Ni) suggests that the bright globular phase may be a solute rich β_r phase as a result of beta phase splitting.

Table 5.3: Summary of EDS spot analysis on the 1150 °C / 70 min. + PB-SCHT + 900 °C 6/24 hr condition near the centerline of the braze zone

	Phase	Ti	Al	Nb	Mo	Ni	Ti/Al	Possible
Condition	No.	(at%)	(at%)	(at%)	(at%)	(at%)	Ratio	Phases
900 °C / 6 hr	A	53.7	40.0	1.8	3.3	1.2	1.34	β_0
	B	49.5	47.1	1.5	1.3	0.6	1.05	γ
	C	57.1	36.7	1.7	2.5	2.0	1.55	?
	D	48.3	39.9	1.6	2.8	7.4	1.21	$\beta_{r,sec}$
900 °C / 24 hr	A	55.2	37.5	1.9	3.7	1.7	1.47	β_0
	B	52.0	43.7	1.5	1.5	1.3	1.19	γ
	C	57.7	37.2	1.6	2.1	1.4	1.55	?
	D	49.3	39.2	1.8	3.1	6.7	1.26	$\beta_{r,sec}$

EDS line scans (Figure 5.9) taken across the bond zone in the PB-SCHT condition

confirm the slight Al-lean bond zone region that spans approximately +/- 600 μm from the centerline of the joint. Additionally, the Mo "spikes" that correspond with the existence of the intercolony multi-phase mixture are evident within the bond zone (Figure 5.9a) and (Figure 5.9b). In addition to Mo partitioning, a slight nickel gradient exists from the centerline of the bond with a maximum nickel content of 1.25 at.% Ni which decreases to less than 0.5 at.% Ni at an approximate distance of 600 μm from the centerline of the bond. Compared with the PB-SCHT condition, a slight relaxation of the overall nickel gradient occurs due to the aging treatment at 900 °C (Figure 5.13). However within the intercolony region, greater partitioning of both Ni and Mo occur within the β_0 phase. Evaluating the peak Ni content across the EDS line scans reveals that the Ni content increases with aging time from a maximum of 2 at.% Ni for the PB-SCHT condition to 3 at.%Ni and 3.8 at.%Ni for the 6 hour and 24 hour ages specimens respectively.

Figure 5.13: SEM-BSE micrographs and associated EDS line scans of the 1150 °C / 70 min. bonded sample subjected to a PB-SCHT heat treatment of 1400 °C for 40 minutes → 11 °C/min to 1280 °C → AQ, followed by aging at 900 °C for (a,b) 6 hours and (c,d) 24 hours.

(a)

(b)

Figure 5.14: Lamellar colony volume fraction versus distance from centerline of the joint for the 1150-70+SCHT condition followed by aging at 900 °C for (a) 6 hours and (b) 24 hours.

(a)

(b)

Figure 5.15: SEM-BSE micrographs of the 1150 °C / 70 min. bonded specimen subjected to a step cooled solutionizing heat treatment of 1400 °C for 40 minutes $\rightarrow$ 11 °C/min to 1280 °C $\rightarrow$ AQ, followed by aging at 900 °C for (a) 6 hours and (b) 24 hours.

5.3.1 Bond Zone Lamellar Colonies

Within the bond zone lamellar colonies, interfacial precipitation of a bright phase is evident within the α_2/γ lath structure for both the 900 °C / 6 hour and 900 °C / 24 hour aged condition (Figure 5.16). For the interfacial precipitates found in the braze zone lamellar colonies, the formation appears similar to $\beta_{0,sec}$ phase precipitates that occur in the parent G2 material when taken through a SCHAT+aging treatment after HIP'ing [40]. The interfacial precipitates appear to form within the α_2 lath at the expense of α_2 lath narrowing and dissolution (Figure 5.16). With increased aging time at 900 °C from 6 hours to 24 hours, the size of the precipitates significantly increase as well as the variability in size based on the near edge-on micrograph (Figure 5.16c). Preliminary EDS spot analysis conducted on the braze zone lamellar colonies is compared against the nominal composition of the lamellar colonies for the substrate material subjected to a SCHAT+ aging treatment at 950 °C for 24 hours. Results indicate the large interfacial precipitates within the bond zone contain a composition high in nickel content compared to the interfacial precipitate in the substrate which contain a high Mo content (Table 5.4). This difference in composition is caused by the increased Ti/Ni and depleted Nb/Mo/Al within the bond zone compared to the parent material. Additionally, Ni is a stronger beta stabilizer compared with Mo, has lower solubility in the alpha phase compared with Mo, and is comparatively more mobile due to the combined substitutional and interstitial diffusion mechanisms within titanium alloys. The result of the enhanced mobility of Ni within the α_2 lath compared to Mo is preferential growth of the nickel rich precipitate to larger sizes in less time compared with a Mo interfacial β_0 phase precipitate. With increasing aging time to 24 hours, the additional fine precipitates shown in Figure 5.17 may possibly be a more conventional Mo rich β_0 phase precipitates, however further study is required to confirm the composition of the fine precipitate in the 24 hour aged condition.

Table 5.4: Summary of EDS spot analysis on the lamellar colonies for the 1150 °C / 70 min. + PB-SCHT + 900 °C / 24 hour condition near the centerline of the braze zone

	Ti	Al	Nb	Mo	Ni	
Phase	(at%)	(at%)	(at%)	(at%)	(at%)	Ref
α_2	51.3	45.5	1.5	1.1	0.7	This Work
γ	50.5	46.3	1.4	1.1	0.7	
PPT	48.3	46.1	1.5	1.1	3.0	
α_2	51.3	42.7	2.9	3.2	0.0	[40]
γ	47.0	50.6	2.4	0.0	0.0	
$\beta_{0,sec}$	48.5	43.7	2.1	6.0	0.0

Figure 5.16: SEM-BSE micrographs of the 1150 °C / 70 min bonded sample subjected to a PB-SCHT followed by aging at 900 °C for 6 hours (a,b), and 24 hours (c,d) showing the near edge on and angled view respectively of the lamellar structure with interfacial precipitates and dissolution of the α_2 lath structure (arrows).

Figure 5.17: EDS spot locations for the 1150 °C / 70 min + PB-SCHT + 900 °C / 24 hour aged condition corresponding to the results of Table 5.4

5.3.2 Substrate Lamellar Colonies

The substrate region subjected to the full bonding, PB-SCHT, and aging treatment is characterized by a near fully lamellar microstructure with lamellar volume fraction on the order of 96-98 vol.%, colony size on the order of 90 μm , with an intercolony region consisting solely of the $\gamma + \beta_0$ phases (Figure 5.18). For both the 6 hour and 24 hour aged condition, the colonies are not well interlocked and the seam width is on the order of 3 μm for both aging times. For the 24 hour aged specimen, both a dark globular intracolony γ phase and a bright globular intracolony β_0 phase are evident in Figure 5.18c. Within the substrate α_2/γ lamellar colonies, an interfacial precipitate is also evident within the α_2 lath structure, and is associated with the precipitation of the β_0 phase on aging. The interfacial precipitates are densely dispersed compared with the parent material subjected to the same thermal treatment prior to bonding [40]. The different growth kinetics are likely caused by the differing cooling rates between the higher air cooled SCHT parent material condition, and the lower intermediate cooling rate of the PB-SCHT specimens. A similar variation in the density of $\beta_{0,sec}$ dispersion was observed for Ti-48Al-2W (at.%) alloys under similar stabilization heat treatments and was attributed to a critical thickness of the α_2 lath structure needed to form stable $\beta_{0,sec}$ nuclei [138]. In that work, thicker α_2 laths as a result of slower cooling from the solutionizing temperature resulted in a denser distribution of $\beta_{0,sec}$ precipitates on aging. Since the α_2 lamellar thickness is greater for the slower cooling rate PB-SCHT condition, a greater density of interfacial $\beta_{0,sec}$ precipitates will occur under the same aging condition as compared with a finer α_2 lath thickness.

Figure 5.18: SEM-BSE micrographs of the parent material microstructure of the 1150 °C / 70 min bonded sample subjected to a PB-SCHT followed by aging at 900 °C for 6 hours (a,b), and 24 hours (c,d) showing the colony boundary morphology and edge on view respectively of the lamellar structure with interfacial precipitates.

5.4 Structure-Property Relationships for Post Bond Heat Treated TiNi Joints: Microhardness

Microhardness measurements were conducted across the PB-SCHT and aged bonds (Figure 5.19). Evident in Figure 5.19 are three main features associated with the microhardness response; (1) the reduction in peak hardness at the centerline of the bond due to the PB-SCHT compared with the as-bonded condition, (2) the reduced hardness gradient across the braze zone for PB-SCHT and PB-SCHT + aged specimens compared with the as-bonded specimen, and (3) the reduced hardness variability across the braze zone with increased aging time at 900 °C for the PB-SCHT+ aged specimens.

For the PB-SCHT specimen, the peak hardness within the braze region has reduced from a value of 540 HV for the as-bonded specimen to 474 HV for the PB-SCHT specimen. On evaluating the location of the peak hardness measurement in the optical microscope, it was determined that the peak hardness measurements for the PB-SCHT condition occur in regions associated within intercolony $\beta_0 + \gamma$ phase regions confined to the braze zone. Previous work has found that β_0 phase regions generally exhibit a deterioration in room temperature strength and ductility [135]. Lamellar colonies generally exhibit a microhardness in the 420-440 HV range, while hardness values less than 400 HV are associated with indent locations containing porosity.

With increased aging time to 6 hours, peak hardness does not significantly decrease, however a slight overall reduction in average hardness and hardness variability is observed (Figure 5.19). Since peak hardness values were not found to increase with aging, it is postulated that the growth of intercolony secondary phases due to the aging heat treatment at 900 °C does not cause embrittlement of the intercolony region within the braze zone. For TNM alloys, the decomposition of the beta phase to form a two phase $\beta_0 + \omega_0$ phase on aging below the ω_0 solvus transition temperature of 825 °C was found to embrittle the intercolony beta phase region [49]. For braze zone microstructures in this work, the intercolony secondary platelet phase that forms does not contribute to an increase in hardness, and therefore assists in the corroboration of this phase as a secondary γ or β_0 platelet. As to the influence of the bright more

Figure 5.19: Microhardness measurements across the bond zone for PB-SCHT and PB-SCHT+Aged specimens compared with as-bonded microhardness at 1150 °C for 70 minutes.

diffuse globular secondary phase that forms within the intercolony region on aging at 900 °C, no significant increase in hardness is observed thus providing further evidence of potential β phase splitting over the formation of the τ_3 phase which should impart a significant influence on hardness as was observed in as bonded specimens containing fine τ_3 precipitates.

Average microhardness measurements of the post-bond heat treated specimens are compared to those of the un-bonded parent material taken through the same SCHT and aging heat treatments (Figure 5.20). Evident in Figure 5.20 is; (1) an overall reduction in average hardness values for all post bond heat treated conditions compared with the parent material subjected to the same heat treatment conditions and, (2) a similar response in hardness reduction due to aging time between parent material hardness and post-bond heat treated hardness. Both phenomena are likely a result of the character of the fully lamellar colonies. As was found for the parent material [40], the reduced hardness for the PB-SCHT material with aging time is attributed to the decomposition of the lamellar structure. Upon SCHT, metastable α_2 laths are present in the microstructure due to relatively fast cooling from the

Figure 5.20: Average microhardness versus aging time at 900 °C for the parent material and PB-SCHT+Aged specimens heat treated at 900 °C compared with as-bonded microhardness at 1150 °C for 70 minutes.

$T_{F/A}$ temperature. With aging at elevated temperature, dissolution of the α_2 lamellae occurs towards equilibrium causing an increase in γ lath volume fraction and the precipitation of an interfacial $\beta_{0,sec}$ precipitate within the α_2 lamellae. Since the α_2 lath is less deformable than both the β_0 and γ phase, as the volume fraction of α_2 lamellae decreases, a proportional decrease in hardness is observed. Additionally, the PB-SCHT microstructure of both the parent material and the bond zone contains a portion of colonies with a coarse lamellar structure. The coarse lamellar structure contains a higher volume fraction of γ lamellae which will impart a lower hardness compared with a fine lamellar structure with higher volume fraction of α_2 lamellae. Furthermore, the fine lamellar colonies have not been characterized in terms of lamellar spacing and lath volume fraction. However, the possibility exists that the slower cooling rate for the PB-SCHT specimens (70-90 K/min) compared with the air cooled parent material may lead to a slightly coarser lamellar structure as is typified by a reduction in cooling rate from heat treatments conducted in the super-transus region for conventional 48-2-2 fully lamellar alloys [139], resulting in lower initial hardness of the PB-SCHT condition compared with the un-bonded parent material condition.

5.5 Summary

As-bonded (1150 °C / 70 minute) specimens were taken through a PB-SCHT and PB-SCHT + aging treatment with a goal of forming a fully lamellar microstructure within the braze zone, while re-forming and stabilizing the fully lamellar microstructure of the parent material prior to bonding. For both PB-SCHT and PB-SCHT + aged specimens, the following significant features were observed;

1. PB-SCHT and PB-SCHT + aged specimens exhibited a graded lamellar volume fraction across the braze zone where the central portion of the braze zone consisted of a near lamellar β microstructure with lamellar colony volume fractions on the order of 75 vol.% within approximately $\pm 300 \mu\text{m}$ of the centerline of the joint.
2. No evidence of the τ_3 phase was found within the microstructure after the PB-SCHT.
3. A graded lamellar colony size ranging from $60 \mu\text{m}$ at the centerline of the braze zone to $90 \mu\text{m}$ in the parent material was realized for both PB-SCHT and PB-SCHT + aged specimens.
4. Upon aging, the intercolony β_0 region within the bond zone exhibited a decomposition reaction whereby the precipitation and growth of two secondary precipitates not previously reported within TiAl diffusion brazed microstructures subjected to post bond heat treatments were found. It is postulated that the bright globular precipitation phase may form via a β phase splitting mechanism, while the identification and formation of the dark platelet phase is inconclusive.
5. Upon aging, both the bond zone and parent material region exhibited the precipitation of an interfacial precipitate within the α_2 lath structure of the lamellar colonies. The bond zone interfacial precipitate is believed to be the β_0 phase which is found to be rich in nickel and experienced significant growth at low aging times. The interfacial precipitate within the parent material is identified as the β_0 phase with expected composition, and exhibited a high density and growth compared with previous studies. The increased interfacial β_0 density within the parent material colonies is attributed to the slower cooling rate from the $T_{F/A}$ temperature compared with air cooling from previous studies.

6. The PB-SCHT condition exhibits a reduction in hardness to 474 HV0.05 compared to the as-bonded condition of 540HV0.05. Further aging resulted in reduced variability in microhardness across the bond zone and a decrease in the average hardness with aging time from 6 hours to 24 hours at 900 °C to approximately 415 HV0.05. The reduced variability in hardness across the bond zone is attributed to a reduction in intercolony hardness as a result of the precipitation of the two unidentified secondary phases. A contribution to the drop in average hardness from the PB-SCHT condition to the 6 hour aged condition is the manifestation of significant interfacial phase precipitation across the entire microstructure.

Chapter 6

Creep Response of P/M Beta Gamma Alloy

6.1 Introduction

To establish a baseline for comparison against creep tests conducted on diffusion brazed + PB-SCHT specimens, high temperature creep tests at 760 °C were performed at constant load initial stress levels of 140 MPa and 276 MPa on the substrate material in the SCHT and SCHT+aged condition. In addition to reporting typical creep parameters, Larson-Miller parameters for each thermomechanical heat treatment were reported at 0.5 % and 1.0 % strain accumulation, as well as rupture time based on the following;

$$LMP = T (20 + \log_{10} (t)) / 1000 \quad (6.1)$$

where LMP is the calculated Larson-Miller parameter, T is the test temperature in degrees Kelvin, and t is the time in hours. Additionally, the “A-Omega” phenomenological model is utilized to characterize strain hardening in the primary creep regime and damage accumulation throughout the tertiary regime [140]. The A-Omega model has been proposed for material systems that exhibit an inflection point in the strain versus creep rate (Figure 6.1) as opposed to systems that exhibit prolonged secondary creep. In this model, the minimum creep rate at a given strain determines the transition from dominant hardening in the region of decelerating strain (primary creep regime), to dominant softening / damage accumulation in the region of accelerating strains (tertiary creep regime). Due to this fact, the strain at the minimum creep rate determines the transition from primary to tertiary creep as is observed for most

Figure 6.1: Definition of parameters associated with the A-Omega model (Equation 6.2) proposed by Clech [140].

engineering alloys including titanium aluminides. The A-Omega model is utilized in this work to characterize the creep response of the parent material condition for beta gamma titanium aluminides. Details of the A-Omega model may be found in [140] where the combined creep rate equation utilized in the A-Omega model is defined as;

$$\dot{\epsilon} = a \cdot e^{-A \cdot \epsilon} + b \cdot e^{\Omega \cdot \epsilon} \quad (6.2)$$

where the first term on the right hand side of Equation 6.2 represents strain hardening in the primary creep regime, and the second term on the right hand side of Equation 6.2 captures strain softening in the tertiary creep regime. Fitting the resultant creep response to the A-Omega model allows a quantifiable comparison of the creep response, the minimum creep rate, the time to reach the minimum creep rate, and a prediction of the time to rupture for various test conditions once the inflection point has been surpassed during a constant load creep test.

6.2 Parent Material Creep Response

The creep response of the parent material under various test conditions is illustrated in Figure 6.2 with pertinent creep properties summarized in Table 6.1. Aging treatments had a marked effect on the creep properties of beta gamma TiAl. Increasing aging time from 0 to 24 hours at 276 MPa has the effect of reducing the instantaneous strain, increasing the primary transient, increasing the minimum creep rate, and reducing overall creep life. The time to 0.5% strain is increased with aging from 0.38 hours for the un-aged sample to 13 hours for the 24 hour aged sample. A similar trend is evident with the time to 1.0% strain (Table 6.1) where an increase from 11 hours to 55.5 hours is observed with increased aging time. The minimum creep rate at 276 MPa increased from $9.03 \times 10^{-9}/\text{s}$ to $1.43 \times 10^{-8}/\text{s}$ between the SHT and 6 hour aged condition, but did not increase with further aging to 24 hours. Overall creep life was detrimentally affected with aging as the SHT condition exhibited time to rupture of 512 hours with a steady decline to 416 hours for the 24 hour aged condition at 276 MPa.

At low applied stress of 140 MPa, the tests were halted after 1375 hours and 300 hours for the SHT and SHT + 900/6hr aged condition respectively. The creep curves exhibit reduced strain rates with aging at a common strain within the primary creep regime. Both tests indicate that strain rates are continuing to reduce even at 1375 hours for the SHT condition, implying that both test conditions are still within the primary creep regime at the halted test time (i.e. have yet to reach the minimum strain rate). As with specimens tested at 276 MPa, a reduction in instantaneous strain with aging led to increased primary strain with aging as is evident by the increase in time to 0.5% strain from 4.33 hours to 73.67 hours for the SHT and SHT + 900/6 hr aged condition respectively. The creep behavior found for the parent material (i.e. improved primary creep with a detriment to overall time to rupture with aging) is similar to γ -Ti-48Al-2W alloys [53], suggesting that the mechanisms involved in the creep performance of both alloys are likely similar and will be detailed in the following sections.

Figure 6.2: Effect of aging time on creep response for the G2 alloys conducted at 760 °C in air with a constant initial stress of 140 MPa and 276 MPa (Note: The SHT specimen evaluated at 140 MPa reached 1375 hours prior to being halted).

Table 6.1: Summary of creep properties of the parent material at 760 °C.

Specimen	Creep	Instantaneous	Time to 0.5%	Time to 1%	Minimum	Creep Life	Rupture
Condition	Stress (MPa)	Strain (%)	Strain (Hours)	Strain (Hours)	Creep Rate (s ⁻¹)	(Hours)	Strain (%)
SCHT	140	0.32	4.33	346	¹ 6.16×10 ⁻¹⁰	—	—
SCHT+ 900/6hr	140	0.29	73.67	—	² 2.27×10 ⁻⁹	—	—
SCHT	276	0.38	0.38	11.0	1.56×10 ⁻⁸	512	14.45
SCHT+ 900/6hr	276	0.30	2.08	38.0	1.81×10 ⁻⁸	463.5	12.25
SCHT+ 900/24hr	276	0.10	13.0	55.5	2.38×10 ⁻⁸	416.0	13.60

¹ Minimum creep rate not achieved, creep rate calculated at 1375 hours.

² Minimum creep rate not achieved, creep rate calculated at 300 hours

6.2.1 Instantaneous Strain

Under high stress at 276 MPa and 760 °C, the parent material exhibits a successive reduction in instantaneous strain with aging from 0.38% for the SHT condition to 0.10% for the SHT + 900 °C / 24 hour aged condition (Figure 6.3). Under low stress at 140 MPa and 760 °C, the parent material exhibits a slight reduction in instantaneous strain with aging from 0.33% for the SHT condition to 0.29% for the SHT + 900 °C / 6 hour aged condition. Instantaneous strain for fully lamellar titanium aluminide materials at high stress has been shown to be related to the heat treatment condition affecting dislocation mobility within lamellar colonies [141,142]. Thus, microstructural parameters associated with the ability to hinder dislocation mobility will influence the instantaneous strain. Prior studies have found that lamellar spacing does not have a significant effect on the ability to hinder dislocation mobility [141]. In the G2 beta gamma alloy, lamellar spacings are roughly 0.04 μm for all aging conditions. With increasing aging time, the α_2 lath volume fraction reduces as a result of α_2 lath dissolution due to the metastable SHT condition. However, the reduction in α_2 lath dissolution for the G2 alloy is accompanied by interfacial beta phase $\beta_{0,sec}$ precipitation at α_2/γ lath boundaries. With increased aging time from 6 hours to 24 hours at 900 °C, $\beta_{0,sec}$ phase precipitation and growth occur at the expense of α_2 lath dissolution resulting in a reduction of instantaneous strain at both 140 MPa and 276 MPa.

The reduction in instantaneous strain is associated with an elastic-plastic strain response. It is likely that the elastic limit has been exceeded for all aging conditions with an applied stress of 276 MPa, and that greater plastic deformation of the unaged condition (i.e. higher instantaneous stress) infers a lower yield strength and/or elastic limit associated with the unaged condition. At 140 MPa, the minor reduction in instantaneous strain implies that an elastic-plastic response may still be operating at 140 MPa and thus the elastic limit for both the aged and unaged condition may be less than 140 MPa at 760 °C. Also, since the instantaneous strain is higher for the unaged condition, we can infer that greater plastic deformation occurs in the unaged specimens at both 140 MPa and 276 MPa. If an elastic-plastic response is operating at both 140 MPa and 276 MPa at 760 °C, we can also infer as in previous studies that the existence of the $\beta_{0,sec}$ precipitates increases the tensile yield strength of the aged condition by preventing dislocation motion along and through lamellar interfaces

Figure 6.3: Effect of aging time on instantaneous creep for the G2 alloys conducted at 760 °C in air with a constant stress of 140 MPa and 276 MPa.

during tensile loading, and that the instantaneous creep strain is dependent on the interface dislocation mobility [141,142]. In the same work, Beddoes et al. [141] has shown that the instantaneous strain is influenced by interfacial precipitates even at low applied stress. In this work, the slight reduction of instantaneous stress associated with aging at 140 MPa indicates that the interfacial beta phase precipitates present in the aged specimen have a minor strain hardening effect on beta gamma titanium aluminides at low applied stress.

Prior studies have indicated that aging will eventually cause excessive α_2 lath dissolution and ripening of the $\beta_{0,sec}$ precipitates leading to an overaging effect similar to Ostwald ripening [142]. For example, for Ti-48Al-2W fully lamellar alloys, aging at 950 °C for 5 hours resulted in a decrease of the instantaneous strain compared with the unaged condition, while aging at 950 °C for 24 hours resulted in an increased instantaneous strain compared with the 5 hour aged condition. For the G2 beta gamma alloy, the instantaneous strain at 276 MPa applied stress continues to decrease with aging time from 0 hours to 24 hours at 900 °C indicating that either an overaging condition has not yet been achieved, or the overaging effect is not resolved based on

Figure 6.4: Effect of aging time on primary creep for the G2 alloys conducted at 760 °C in air with a constant stress of 140 MPa and 276 MPa.

the selected heat treatment times of 6 hours and 24 hours.

6.2.2 Primary Creep

Primary creep properties for the parent material at 760 °C are summarized in Table 6.2 and shown in Figure 6.4. The time to reach 0.5% creep strain and 1.0% creep strain increases with aging time, while the absolute strain levels after 24 hours reduces with increased aging time at 900 °C. The increase in time to reach various primary creep strain levels is aided by the reduction in instantaneous strain from the SCHT condition to the aged conditions, as well as the faster decrease in strain rate that is observed immediately following the instantaneous portion of the creep response (Figure 6.5).

The primary creep response in fully lamellar TiAl alloys is primarily attributed to lamellar size, lamellar spacing, and the presence, morphology, distribution and

Table 6.2: Summary of primary creep properties of the parent material at 760 °C.

Specimen	Creep	Time to 0.5%	Time to 1%	Strain at	Min Strain	Strain at min	Time to min
Condition	Stress (MPa)	Strain (hr)	Strain (hr)	24 hours (%)	Rate (/s)	Strain Rate (%)	Strain Rate (hr)
SCHT	140	4.33	346	0.61	³ 6.16×10^{-10}	—	—
SCHT+ 900/6hr	140	73.67	—	0.41	⁴ 2.27×10^{-9}	—	—
SCHT	276	0.38	11.0	1.16	1.56×10^{-8}	1.77	117.8
SCHT+ 900/6hr	276	2.08	38.0	0.87	1.81×10^{-8}	1.49	99.0
SCHT+ 900/24hr	276	13.0	55.5	0.63	2.38×10^{-8}	1.17	75.0

³ Minimum creep rate not achieved, creep rate calculated at 1375 hours.

⁴ Minimum creep rate not achieved, creep rate calculated at 300 hours

Figure 6.5: Effect of aging time on strain rate immediately following instantaneous creep for the G2 parent material alloy conducted at 760 °C in air with a constant stress of 140 MPa and 276 MPa.

stability of interfacial precipitates. All of these factors influence the emission and motion of dislocations along lamellar interfaces. As metastable α_2 laths decompose on heating, the α_2 laths may become thin and/or discontinuous due to the migration of α_2/γ interfaces and the precipitation of $\beta_{0,sec}$ precipitates within the α_2 lath structure. A consequence of α_2 lath thinning and discontinuity is a coarsening of the γ lamellae. The coarsening of γ laths allows less restricted movement of dislocations leading to increased primary creep strain. To counteract the effects of discontinuous α_2 lath dissolution, aging prior to creep has been shown to stabilize the α_2 lath structure and precipitate the interfacial $\beta_{0,sec}$ precipitates resulting in improved primary creep response [50, 142]. For the G2 alloy aged at 900 °C for 6 hours and 24 hours, the α_2 lath morphology remains relatively continuous while the beta phase precipitates continue to coarsen with aging time [40]. The aged conditions exhibit both a lower instantaneous strain, and a faster decrease in strain rate (Figure 6.5) leading to greater times to 0.5% creep strain and 1.0% creep strain. The time to 0.5% and 1% strain at 276 MPa reveals that beta phase precipitate coarsening and the continuous nature of the α_2 lath structure assist in reducing primary creep strain with aging time at 900 °C up to 24 hours.

For creep tests conducted at 140 MPa and 760 °C, the minimum creep rate is not yet reached after 1375 hours, however the reduced primary-creep transient strain with aging is likely caused by the same stabilizing effect associated with the creep response at 276 MPa. Primary creep response at 140 MPa in the SHT condition is characterized by a strain rate of 6.16×10^{-10} /s at 0.98% strain in 1375 hrs, while the SHT + 900/6 hr condition is characterized by a strain rate of 2.27×10^{-9} /s at 0.74 % strain in 300 hours. A faster reduction in strain rate immediately following instantaneous strain is evident for the aged condition through Figure 6.5 and the A-Omega fit parameters (Figure 6.6 and Table 6.3). The SHT+aged sample exhibits a similar response as the SHT sample except the response occurs at a lower primary creep strain, which for the 276 MPa condition, was shown to produce a lower primary creep transient strain and higher minimum strain rate.

Since the time to 1% strain was not achieved at 140 MPa, a Larson-Miller plot was generated for both the time to 0.5% strain and 1.0 % strain (Figure 6.7). The trend in Larson-Miller parameter (LMP) was shown to increase with aging time at both stress levels indicating the improvement in primary creep response. Compared against

Figure 6.6: A-Omega model fit for the parent material in the (a) SCHT, (b) SCHT+6hr, and (c) SCHT+24hr aged condition

Table 6.3: Summary of A-Omega fit parameters for constant load creep tests conducted on the parent material at 760 °C

Specimen	Creep Stress	a	A	b	Ω	R^2
Condition		/sec		/sec		
SCHT	140	1.41×10^{-04}	1585	—	—	0.9810
SCHT+ 900/6hr	140	0.435	4764	—	—	0.9910
SCHT	276	7.35×10^{-06}	450	8.45×10^{-06}	36.16	0.9924
SCHT+ 900/6hr	276	1.93×10^{-06}	510	1.13×10^{-08}	36.03	0.9920
SCHT+ 900/24hr	276	4.44×10^{-07}	575	1.83×10^{-08}	30.02	0.9948

other experimental titanium aluminide alloys in the aged condition, the G2 alloy processed through a P/M route exhibits primary creep properties within the same performance bracket as other near fully lamellar titanium aluminides. As expected, increased aging time to 24 hours at 900 °C produces the highest LM-parameters. As with other experimental alloys, thermo-mechanical processing of the G2 beta gamma alloy imparts a significant effect on resultant primary creep response, and a full optimization of the G2 alloy for primary creep response may impart greater performance than that shown in this work.

(a)

(b)

Figure 6.7: Larson-Miller parameter for the G2 parent material alloy at 760 °C and (a) 0.5 % creep strain and, (b) 1.0 % creep strain compared against other experimental TiAl alloys (Ti-44.5Al-6.25Nb-0.8Mo-0.1B [143], Ti-43.5Al-4Nb-1Mo-0.1B-0.5C [144], Ti-43.5Al-4Nb-1Mo-0.1B [28], Ti-48Al-2W [142], Ti-45Al-5Nb-5Zr-0.2B-0.2C [31], Ti-48Al-2Cr-2Nb-1W [145], Ti-45Al-2W-0.6Si-0.7B [146])

6.2.3 Minimum Creep Rate

For creep tests conducted at 760 °C and 276 MPa, all tests were taken to rupture and the full log-linear plot of strain rate versus strain is characterized (Figure 6.8). At 140 MPa and 760 °C, the SHT specimen was allowed to creep for 1375 hours, while the SHT+ 900 °C / 6 hour aged specimen was halted after 300 hours. For both specimens, the log linear plot of strain rate versus strain data only shows a region of decelerating strain and thus only the primary part of the A-Omega model is fitted to the experimental data, even though the minimum strain rate has not yet been achieved (Table 6.3, Figure 6.9).

The minimum creep rate (Figure 6.8) for the 276 MPa condition indicates that as aging time increases at 900 °C, the magnitude of the minimum creep rate increases slightly from 9.03×10^{-9} /s to 1.43×10^{-8} /s but occurs at a reduced creep strain. The rate of strain rate decrease within the primary creep regime is higher for the aged condition compared with the unaged condition as indicated by increasing slope as quantified through the “A” parameter via the A-Omega model which indicates an increase in slope from 450 to 575 as aging time increases at 900 °C (Figure 6.10). For the unaged condition, the absolute value of the minimum strain rate is lower than that of the aged condition resulting in a prolonged primary transient to 118 hours even though the primary transient occurs at a higher absolute strain level of 1.77%. On the contrary, aged specimens exhibit a primary transient occurring at 1.49 % and 1.17% strain for the SHT+6 and SHT+24 hour aged specimens respectively.

Figure 6.11 shows the microstructure within the gauge length of the unaged sample after creep rupture. Evident in Figure 6.11 is the precipitation and growth of interfacial $\beta_{0,sec}$ precipitates which is not evident in the microstructure prior to creep testing. The prolonged primary transient for the unaged condition is a result of the dynamic precipitation of these interfacial $\beta_{0,sec}$ precipitates that manifest during creep testing at 276 MPa and 760 °C, and is a known mechanism for enhancing creep resistance in fully lamellar titanium aluminide alloys [50].

For samples subjected to a creep stress of 140 MPa at 760 °C, the creep response is still within the primary creep regime after 1375 hours of accumulated creep damage

Figure 6.8: Effect of aging time and stress level on creep rate for the G2 alloys conducted at 760 °C in air with a constant stress of 140 MPa and 276 MPa.

and the strain rate has not yet have reached a minimum based on continued decelerating strain rates for both SHT and SHT + aged condition. Therefore the strain rate computed at 300 hours is utilized for comparison purposes. The minimum creep rate found for the 140 MPa condition at 300 hours is 2.69×10^{-9} /s and 2.19×10^{-9} /s for the unaged and 900°C / 6 hour aged specimens respectively. Evident in the creep response is the greater strain rate decrease for the aged condition over the unaged condition (Figure 6.5 and Figure 6.8). This phenomena is caused by the pre-existence of the interfacial $\beta_{0,sec}$ precipitates that have been stabilized by the aging treatment prior to the creep test. For the unaged condition, an incubation period is required before nucleation of the interfacial precipitates will occur at 760 °C, and hence the strain rate does not drop as quickly, but will likely reach a lower minimum rate as in the 276 MPa case once the interfacial $\beta_{0,sec}$ precipitates have growth to a size that influences dislocation motion through the lath structure.

Both the stress dependence and influence of thermomechanical treatment on the A-Omega model parameters associated with the primary creep regime are evaluated (Figure 6.12). From the Alpha parameter fit (Figure 6.12a), an increase in stress level

Figure 6.9: A-Omega model fit for the parent material in the (a) SCHT, (b) SCHT+6hr aged condition at 760 C and 140 MPa.

is associated with a decrease in the Alpha parameter for a given thermomechanical condition. The alpha parameter models the slope of the strain rate decrease in the primary creep regime. As expected, the alpha parameter is inversely proportional to stress level, but varies depending on thermomechanical treatment for the G2 alloy and exhibits significant contrast at the lower stress level of 140 MPa compared with 276 MPa. This contrast reveals a greater sensitivity of the thermomechanical treatment during long term creep testing at low stress levels. Additionally, for constant creep stress of 276 MPa, the primary creep factor “a” is shown to decrease with increasing minimum strain rate (Figure 6.12b), which in this case is directly correlates with aging time at 900 °C. This trend is indicative of the impact of the instantaneous strain that is lower for specimens aged at 900 °C. The lower instantaneous strain for the aged condition shifts the response to lower overall strain levels resulting in a lower primary creep factor with aging time at 900 °C. As found in the literature [140], the linear dependence of the primary creep factor with minimum strain rate indicates the strong dependence of the minimum creep rate on the entire creep curve.

Figure 6.10: Alpha Parameter versus aging time at 900 °C for creep tests conducted at 760 °C.

(a)

(b)

Figure 6.11: SEM-EDS micrographs of the SCHT specimen after creep rupture at 276 MPa and 760 °C showing the dynamic precipitation of interfacial $\beta_{0,sec}$ precipitates in the (a) gauge section and (b) threaded section of the creep sample.

(a)

(b)

Figure 6.12: (a) Alpha parameter versus creep stress for the SCHT and SCHT + 900 °C / 6 hour aged condition, (b) Primary creep factor “a” versus minimum strain rate for specimens crept at 276 MPa and 760 °C.

6.2.4 Tertiary Creep & Deformed Microstructures at Rupture

Previous studies [147–150] have shown that microstructure plays a significant role in the deformation mechanisms and resultant tertiary creep properties of polycrystalline fully lamellar TiAl alloys. Fully lamellar alloys exhibit the greatest creep resistance of polycrystalline TiAl alloys. The primary mechanisms associated the superior creep resistance of fully lamellar alloys is the fine lamellar spacing as well as interfacial phase particles present at the lamellar interfaces which hinder dislocation emission and motion during high temperature creep [148]. Additionally, a well interlocked colony boundary morphology with minimal globular intercolony grains has been shown to improve creep resistance. Therefore, by suppressing intergranular phases, maintaining the fully lamellar well interlocked microstructure, and inducing interfacial precipitates, creep resistance is improved.

Void formation may occur through the delamination of the lamellar microstructure or through intergranular void initiation, coalescence, and eventual cracking. If coarse globular $\beta_0 + \gamma$ grains exist at the colony boundaries, a more rapid onset of tertiary creep typically occurs. The rapid onset of tertiary creep is attributed to the initiation and formation of intergranular voids within the globular particles since the highly resistive lamellar structure will oppose fracture more readily compared with the softer β_0 phase at high temperature. Therefore, the stability of intercolony phases during exposure to elevated temperature and stress such as those exhibited during high temperature creep may play a crucial role in the overall time to rupture. Also, since the load is carried principally by the grain boundary region, the additional loss of well interlocked lamellar grains due to intercolony phase coarsening may promote the acceleration of grain boundary damage accumulation leading to earlier rupture times [151]. Additionally, within the colonies themselves, longitudinal and lateral dissolution of individual laths, as well as the coarsening of interfacial particles may reduce the effectiveness of blocking dislocation emission and motion leading to reduced creep performance.

In addition to the the presence and instability of $\beta_0 + \gamma$ intercolony phases as a detrimental aspect associated with tertiary creep performance, other experimental beta gamma alloys containing beta stabilizers such as those of the TNM system may exhibit intercolony decomposition of the β_0 phase. The decomposition of the β_0 phase to an ω or ω_0 phase occurs, which has been found to embrittle the alloy during creep

deformation at high temperature. In those studies, the ω_0 phase manifests due to the high nominal Nb content within the β_0 phase that promotes ω_0 stabilization at temperatures on the order of 775 °C [49]. A slight change in Nb/Mo content within the β_0 phase has an opposing effect causing stabilization of the β_0 phase.

The G2 alloy in this work exhibits different intercolony character depending on the aging heat treatment applied prior to creep strain. For the alloy utilized in this work, the intercolony region in the SHT condition exhibits a very small volume fraction of equiaxed $\beta_0 + \gamma$ phases. The volume fraction of these phases are less than 1 vol% in the SHT condition and increases with increasing aging time at 900 °C to approximately 6 vol.% after 24 hours of ageing. Additionally, the SHT condition exhibits a mixture of well interlocked and planar boundary morphology, which is known to provide excellent deformation resistance within the tertiary creep regime [8]. The stability of the well interlocked colony boundary morphology changes to a more planar morphology as the intercolony region coarsens during heat treatment at 900 °C and potentially during creep testing at 760 °C, and thus, some impact on tertiary creep response is expected.

Based on the overall creep curves (Figure 6.2) and creep summary data (Table 6.1), the creep life of the SHT condition at 276 MPa is 512 hours which decreases with aging time to 463 hours and 413 hours for the 6 hour and 24 hour aged condition respectively. Overall, the G2 alloy in the SHT condition exhibits better creep life than the aged conditions. However, better primary creep resistance was achieved in the aged conditions. This behavior can be attributed mainly to the presence, in the G2 alloy, of the $\beta_{0,sec}$ precipitates at the lamellar interfaces as well as at the grain boundaries, even though the lamellar grain size is relatively fine. The improved primary creep resistance of the aged conditions is beneficial towards the adoption of titanium aluminides for gas turbine blade applications. In gas turbine blade applications, the maximum allowable creep strain is on the order of 1 % with acceptable creep strain rates on the order of $1 \times 10^{-8} s^{-1}$ in order to achieve a service interval of approximately one year [8]. Thus the primary creep response of the aged condition is a more attractive microstructure from a turbine blade design standpoint.

Figure 6.13 shows the deformation microstructures of crept samples in the SHT, 6 hour, and 24 hour aged conditions with the applied load in the vertical direction. It shows substantial voids formed and coalesced at colony boundaries where coarse intercolony $\beta_0 + \gamma$ grains were observed for all aging conditions. Intergranular voids

occur along colony boundaries oriented near the 45 degree direction to the loading axis where the shear stress is known to be at a maximum. These voids nucleated at grain boundaries transverse to the loading direction, grew, and coalesced into cracks leading to fracture. During creep, colony growth did not occur for the near fully lamellar structures, however, dynamic growth of equiaxed $\beta_0 + \gamma$ phases is evident along lamellar grain boundaries, especially in the aged conditions as shown in Figure 6.13e and Figure 6.13h.

The volume fraction, size, and stability of intercolony phases likely play a role in the tertiary creep response. Given the variation in creep rupture times, each condition was subjected to a variation in thermal exposure at 760 °C so a direct comparison of the dynamic growth rate of each condition is not possible. However, the volume fraction of the intercolony phases has increased for the 24 hour aged condition during creep as shown in Figure 6.14. An increase in intercolony $\beta_0 + \gamma$ phases to approximately 17.5-23 vol.% occurs depending on the aging condition and the final volume fraction at rupture is comparable for all three conditions. However, in the aged condition, these equiaxed intercolony $\beta_0 + \gamma$ grains coarsened during creep as shown in Figure 6.13e,f,h and i. Previous studies indicated that tertiary creep strain in the aged Ti-48Al-2W alloy predominantly occurred in lamellar grain boundary regions, producing extensive dislocation and twinning activity, and causing local hardening and strain discontinuities across grain boundaries [147,148]. Eventually, the presence of the relatively coarse intergranular grains acted as an effective void initiation sites leading to the formation of intergranular voids during tertiary creep. Similarly, in the aged G2 alloys the propensity for intergranular void formation increased during tertiary creep due to coarsening of intercolony $\beta_0 + \gamma$ grains at lamellar grain boundaries. Therefore, the more extensive tertiary creep and longer creep life of the SHT sample is a result of more balanced accommodation of creep strain between lamellar and intercolony regions. In contrast, for the aged samples, larger intercolony $\beta_0 + \gamma$ grains, a slightly higher volume fraction of intercolony $\beta_0 + \gamma$ grains, and a more resistant lamellar structure with coarsened interfacial $\beta_{0,sec}$ precipitates resulted in reduced tertiary creep life even though there was an improvement of primary creep resistance.

For the G2 alloy, no evidence of the ω_0 phase was evident within intercolony β_0

Figure 6.13: Deformed microstructures of the (a-c) SHT, (d-f) 6 hour and (g-i) 24 hour aged condition after rupture at 276 MPa and 760 °C. Loading direction is vertical with respect to all micrographs.

Figure 6.14: Volume fraction of intercolony $\gamma+\beta$ phase versus aging time after creep.

phase after creep rupture indicating that β_0 phase for the G2 alloy is thermodynamically stable at 760 °C for at least 500 hours at 276 MPa. Beneficial aspects of the G2 alloy in this study are related to the finely dispersed mixture of $\beta_0 + \gamma$ at colony boundaries that minimizes islands of β_0 grains at colony boundaries or triple points. The colony boundary morphology along with the nominal Mo content within the alloy suppress ω_0 phase decomposition during high temperature creep deformation.

In addition to the dynamic intercolony growth during creep testing, the deformed microstructures also exhibit changes in lamellar morphology. Both a wavy lamellar appearance and lamellar coarsening for all three aged conditions was evident and is shown in Figure 6.15. The appearance of lamellar coarsening has been attributed to α_2 and γ/γ dissolution driven by the emission of interfacial dislocations and ledge deformation in γ -TiAl [147]. Extensive lamellar deformation due to dislocation activity and twinning at the coarse lamellae may result in wavy lamellae and eventually lead to lamellar delamination.

When comparing the LMP for time to rupture as shown in Figure 6.16, a reversal in performance is observed with the SHT heat treatment providing the longest time to rupture in the G2 alloy compared with the aged condition. At the same stress level,

Figure 6.15: OM micrograph of the beta gamma TiAl (G2) in the SHT condition after creep rupture with wavy lamellae in the colonies.

although the Ti-48Al-2W alloys [50] exhibits higher performance of rupture life, the G2 alloys perform adequately compared with other experimental titanium aluminide alloys.

The influence of thermomechanical treatment on the A-Omega model parameters associated with the tertiary creep regime are evaluated (Figure 6.17). From the Omega parameter fit (Figure 6.17a), an increase in aging time is associated with a decrease in the omega parameter. Other studies have found that with increasing creep stress and/or increasing minimum strain rates, the omega parameter decreases which is consistent with the results of the G2 alloy at 760 °C and 276 MPa. The rupture strain remains relatively similar between aging conditions at 276 MPa and 760 °C, however, the onset of the tertiary creep regime varies with both minimum strain rate and absolute strain. For the SHT condition, the minimum strain rate is lower and at a higher absolute strain compared with the aged conditions. Therefore with a similar rupture strain between all aging conditions, the SHT condition will exhibit the highest omega parameter.

Additionally, for constant creep stress of 276 MPa, the tertiary creep factor “b” is shown to increase with increasing minimum strain rate (Figure 6.17b), which in this case is proportional with aging time at 900 °C. This trend is indicative of the impact

Figure 6.16: Comparison of time to rupture for G2 beta gamma TiAl with other experimental γ -TiAl and $\beta - \gamma$ -TiAl (Ti-44.5Al-6.25Nb-0.8Mo-0.1B [143], Ti-43.5Al-4Nb-1Mo-0.1B [28], Ti-43Al-4Nb-1Mo-0.1B-0.3C-0.3Si [144], Ti-43Al-4Nb-1.5Mo-0.1B-0.5C [144], Ti-48Al-2W [142], Ti-48Al-2Cr-2Nb-1W [145], Ti-46Al-8Ta [152]).

Figure 6.17: (a) Parameter Omega versus aging time for parent material creep tests conducted at 276 MPa and 760 °C, (b) Tertiary creep factor 'b' versus minimum strain rate for creep tests conducted at 276 MPa and 760 °C.

of the onset of the tertiary creep inflection point that is shifted to lower absolute strain values for the aged conditions. The lower absolute strain inflection point for the aged conditions shifts the response to lower overall strain levels resulting in a higher tertiary creep factor with aging time at 900 °C.

Departure from the A-Omega model occurs for all three conditions between the minimum strain rate inflection point and the time to rupture. Between approximately 8-10 % creep strain, the strain rate departs from the linear fit of the A-Omega model to lower strain rate values. This departure in fit appears more prominent for the SHT condition compared with the aged conditions. With increased aging, a reduction of the departure from the model is observed and is likely a result of the stabilization heat treatment. The phenomena associated with this model departure requires further investigation but speculation of a mechanism change in the late stages of damage accumulation is suspected where a balance in void formation and coalescence may temporarily give way to lamellar deformation and potential lamellar delamination. Since the SHT condition is somewhat more microstructurally unstable compared with the aged condition, continued microstructural changes to both intercolony regions and within the lamellar colonies may impart a variance in the tertiary creep deformation mechanism in the latter stages of the tertiary creep regime.

6.3 Creep Response of Diffusion Brazed Powder Metallurgy Beta Gamma Titanium Aluminide Alloy

The influence of diffusion brazing process parameters as well as PBHT thermal treatments on the creep properties of diffusion brazed titanium aluminides is not well understood due to sparse experimental data available in the literature. For diffusion brazed titanium aluminides, it is realized that the diffusion brazing process may contribute to additional defects associated with the solidification phenomena that may be detrimental to their performance, thus limiting their potential use. Some additional defects possible during the diffusion brazing and PBHT thermal cycle include: (1) compositional variation due to the selected interlayer material and brazing thermal cycle that manifest as detrimental lamellar colony or intercolony microstructural

features, and (2) the manifestation of microporosity due to a number of factors including liquid run out of the joint, incomplete joint filling, or volume contraction on cooling. The microporosity defect may act to reduce the load bearing cross section of the creep sample as well as act as crack nucleation sites. It has been found that the size, quantity, and distribution of pre-existing porosity in both cast and P/M metallic components will impact both the rupture time and rupture strain [31,153,154]. Since the nucleation, growth, and coalescence of voids usually occurs at grain boundaries, pre-existing porosity eliminates the need to nucleate voids from collections of vacancies which leads to a randomizing time to failure based on the morphology of the porosity field [155]. Optimization of the diffusion brazing parameters are required in order to reduce such defects and improve the mechanical properties of diffusion brazed titanium aluminides. In order to better understand the influence of the diffusion brazing thermal cycle and associated PBHT on the creep properties of P/M beta gamma alloys, preliminary constant load creep tests are conducted based on selected diffusion brazed thermal cycle conditions that produced the most attractive microstructure compared with the parent material microstructure prior to diffusion brazing.

Diffusion brazed specimens in the SCHAT and SCHAT + aged condition were subjected to constant load creep tests at 140 MPa, 208 MPa, and 276 MPa at 760 °C. The diffusion brazing bonding cycle conducted at 1150 °C for 70 minutes followed by a PB-SCHAT heat treatment of 1400 °C for 40 minutes followed by cooling at 11 °C/min to 1280 °C followed by air cooling was selected along with the same condition subjected to aging at 900 °C for 6 hours. These conditions were selected due to their minimal segregation and microhardness variation across the diffusion brazing zone, relatively high volume fraction of lamellar colonies, minimal intercolony seam width for the PB-SCHAT condition, and existence of interfacial precipitates that were evident for the aged condition at 900 °C for 6 hours.

Prior to creep testing two PB-SCHAT + 900 °C / 6 hour specimens were subjected to microcomputed tomography (microCT) scans. These microCT scans were conducted to elucidate the impact of braze porosity on creep response. A centerline microCT image of the centerline porosity is shown in Figure 6.19 and Figure 6.18 for each sample. Volume fraction measurements based on microCT volume rendering was conducted across the gauge length for each sample (Figure 6.20). Evident in Figures 6.19 through 6.20 is the variation of centerline porosity, with an increase in

Figure 6.18: MicroCT image at the centerline of the bond for the PB-SCHT + 900 °C 6 hour aged condition (Sample #1 - LP) prior to creep testing.

overall porosity volume fraction for sample #2 over sample #1. A maximum center-line porosity level of 4 vol% occurred for sample #1 (Low Porosity - LP) and 18 vol% for sample #2 (High Porosity - HP) respectively. The greater level of porosity in the centerline of the bond is difficult to explain as the bonding procedure and conditions were nearly identical for each sample. The resultant variation in porosity points to the importance of faying surface preparation, bonding jig/fixture design, joint design, and environmental conditions for joining titanium aluminide alloys. The influence of variation in porosity volume fraction for these two samples will be compared at a low applied creep stress level of 140 MPa at 760 °C.

The creep response of the diffusion brazed material under various test conditions is illustrated in Figure 6.21 with pertinent creep properties summarized in Table 6.4. The diffusion brazing process had a marked effect on the creep properties of beta gamma TiAl. Instantaneous strains varied with a reduction of instantaneous stress with aging at 140 MPa. Primary creep response at low stress of 140 MPa

Figure 6.19: MicroCT image at the centerline of the bond for the PB-SCHT + 900 °C 6 hour aged condition (Sample #2 - HP) prior to creep testing.

was impacted by both PB-SCHT condition and level of pre-existing porosity in the braze zone. With increasing creep stress for the PB-SCHT condition, minimum strain rates increased from 2.28×10^{-9} /s to 1.8×10^{-8} /s as expected with a reduction in the onset of tertiary creep as the applied stress increased from 140 MPa to 276 MPa. Additionally, the tertiary creep regime was very short for intermediate (208 MPa) and high stress (276 MPa) conditions leading to reduced time to rupture of 47-110 hours and rupture strains less than 2.5 %.

Figure 6.20: Porosity volume fraction versus distance from the centerline of the bond for two specimens brazed at 1150 °C for 70 minutes, followed by a PB-SCHT of 1400 °C 40 min 11 °C/min cooling to 1280 °C followed by air cooling, then subjected to an aging heat treatment of 900 °C for 6 hours. Specimens were further subjected to constant load creep tests at 140 MPa and 760 °C.

Table 6.4: Summary of creep properties of the diffusion brazed G2 material at 760 °C.

Specimen Condition	Creep Stress (MPa)	Instantaneous Strain (%)	Time to 0.5% Strain (Hours)	Time to 1% Strain (Hours)	Minimum Creep Rate (s ⁻¹)	Creep Life (Hours)	Rupture Strain (%)
PBSCHT	140	0.52	0.0057	295.8	⁵ 2.28×10 ⁻⁹	–	–
PBSCHT+ 900/6hr LP	140	0.27	111.5	–	⁶ 1.97×10 ⁻⁹	–	–
PBSCHT+ 900/6hr HP	140	0.18	14.17	258.5	⁷ 3.10×10 ⁻⁹	–	–
PBSCHT	208	0.27	3.10	51.42	8.03×10 ⁻⁹	221.8	1.71
PBSCHT S01	276	0.37	0.56	7.0	2.72×10 ⁻⁸	46.5	1.79
PBSCHT S02	276	0.44	0.11	6.08	1.80×10 ⁻⁸	104.1	2.35

⁵ Minimum creep rate not achieved, creep rate calculated at 300 hours.

⁶ Minimum creep rate not achieved, creep rate calculated at 300 hours

⁷ Minimum creep rate not achieved, creep rate calculated at 300 hours

Figure 6.21: Effect of aging time on creep response for the diffusion brazed G2 alloys conducted at 760 °C in air with a constant stress of 140 MPa, 208 MPa, and 276 MPa.

6.3.1 Instantaneous Strain

Bonded conditions reveal some anomalies in instantaneous strain compared with the parent material condition. Generally speaking, the instantaneous strain decreases with decreasing creep stress for bonded conditions with the exception of the PBSCHT condition at 140 MPa (Figure 6.22). This condition produced a high instantaneous strain of over 0.5 % and is difficult to explain. For other bonded conditions, instantaneous strains at 140 MPa are generally within the 0.2-0.3 % creep strain, while the bonded condition at 276 MPa condition produces instantaneous strains on the order of 0.4 %. For the bonded condition, the instantaneous strain is not necessarily higher than the parent material condition for the same heat treatment (Figure 6.23). The difference in instantaneous strain is attributed to a number of possible factors. The first factor is that the impact of the bonding thermal cycle and additional heat treatment altered the substrate material within the gauge length such that the elastic-plastic response is altered compared with the parent material. The elastic-plastic response is altered through microstructural changes associated with the internal colony structure, a colony size change, and/or colony boundary morphology.

Figure 6.22: Effect of aging time on instantaneous creep for the diffusion brazed G2 alloys conducted at 760 °C in air with a constant stress of 140 MPa, 208 MPa, and 276 MPa.

A correlation between yield strength and instantaneous strain has been determined for fully lamellar alloys with interfacial precipitates whereby the existence of interfacial precipitates increases the tensile strength at high temperature while reducing the instantaneous strain [141,142]. Secondly, the near lamellar microstructure within the bond region may contribute to a change in instantaneous strain as reducing the lamellar colony volume fraction may alter the yield strength of the material as has been found for near lamellar and duplex microstructures compared with fully lamellar microstructures [143,156]. Thirdly, the presence of porosity in the bond may reduce the effective cross sectional area causing greater localized applied stress in the bond region resulting in a greater instantaneous strain response. Such a response is the primary candidate for the high instantaneous strain response for the PB-SCHT condition at 140 MPa even though the level of porosity is unknown. Fourthly, the composition within the bonded region is aluminum depleted and may contribute to a change in instantaneous creep response since low aluminum content on the order of 42 at.% is known to increase yield strength at the expense of elongation for both

Figure 6.23: Comparison of instantaneous creep strain between the diffusion brazed + PBHT material and parent material conducted at 760 °C in air. Sample #1 and #2 for the 140 MPa + aged condition refers to the low porosity and high porosity bonds respectively.

conventional and experimental titanium aluminides [8].

6.3.2 Primary Strain and Minimum Strain Rate

Primary creep response, strain rate versus strain, and pertinent primary creep results are shown in Figures 6.24, Figure 6.25, and Table 6.4 respectively. With increasing applied stress from 140 MPa to 276 MPa for the PB-SCHT condition, the minimum creep rate increases as expected and is extended to higher creep strain even though the 140 MPa condition experienced significant instantaneous strain. Under the high stress conditions of 276 MPa, both PB-SCHT samples exhibit a similar primary creep response, and compared with the parent material (Figure 6.26b), the bonded specimen #2 exhibits a similar minimum strain rate and onset of tertiary creep strain of 1.8×10^{-8} /s at 1.8 % strain, while specimen #1 exhibits an increased minimum strain rate of 2.72×10^{-8} /s, at a lower strain level of 1.55 %. The main difference between the bonded specimens and parent material within the primary creep regime is the strain rate decrease. Evident in Figure 6.26b is a cross-over in strain rate at approximately 0.65 % strain, where the parent material exhibits a more pronounced reduction in strain rate leading to a longer time to the minimum strain rate (i.e. onset of tertiary creep) of 94 hours at 1.75 % strain compared to 60 hours at 1.8 % strain for the bonded condition (Sample #2). Since instantaneous strain between the bonded and parent material condition are quite similar, the primary creep response is not impacted by instantaneous strain between the bonded condition and parent material condition.

As characterized in Chapter 5, the bonded PB-SCHT condition exhibits a reduced lamellar volume fraction of approximately 75 vol.% near the centerline of the bond, as well as possible reduced interlocked colony boundaries and slightly coarser lamellar spacing due to the slower cooling rate. It is speculated that a combination of reduction lamellar colony volume fraction and coarser lamellar spacings contributes to the increase in creep rate during the primary creep regime of the diffusion brazed specimens as has been confirmed for other near fully lamellar titanium aluminides [157]. When reviewing the deformed lamellar structure for the PB-SCHT bonded condition crept at 276 MPa (Figure 6.27), evident are the existence of coarse lamellar colonies (Figure 6.27a), but with a well maintained lamellar structure when the colonies are fine (Figure 6.27b,c) with little to no discontinuous coarsening, and the evidence of

Figure 6.24: Primary creep response for the G2 alloys diffusion brazed and PBHT at 760 °C in air with a constant stress of 140 MPa, 208 MPa, and 276 MPa.

limited dynamic interfacial $\beta_{0,sec}$ precipitation at the lamellar interfaces. The lamellar structure within the diffusion brazed colonies appear somewhat stable, with the possibility of less dynamic interfacial precipitation compared with the parent material when subjected to creep stress 276 MPa and 760 °C. However, a direct comparison is difficult as the rupture time is significantly less (i.e. 47 hours) compared with the parent material rupture time (i.e. 512 hours) and may not be considered a direct comparison of the evolution of dynamic precipitation at the lamellar interfaces. Thus, the likelihood of coarse lamellar colonies, the possibility of reduced dynamic precipitation, and a high degree of structural inhomogeneity [8] due to the variation in microstructure between the braze zone and parent material that has been found to expand primary creep response, and are the main contributing factors of the primary creep expansion for the diffusion brazed condition.

Under a low stress condition of 140 MPa, the PB-SCHT condition exhibits a similar strain rate decrease as the parent material (Figure 6.28b), but since the instantaneous strain is higher, the time to 0.5 % creep strain is significantly shorter (Figure

Figure 6.25: Strain rate versus strain for the G2 alloys diffusion brazed and PBHT at 760 °C in air with a constant stress of 140 MPa, 208 MPa, and 276 MPa.

6.28a). Evident in Figure 6.28b is the similar strain rate and cumulative creep strain at 300 hours for the PB-SCHT condition compared with the parent material in the un-bonded SCHT condition (i.e. 2.28×10^{-9} /s at 0.92% strain for the bonded condition, and 2.28×10^{-9} /s at 0.96 % strain for the parent material SCHT condition). Based on short term creep tests at 140 MPa, the impact of diffusion brazing the G2 alloy with the specific thermal cycle and interlayer material on the PB-SCHT material appears to be confined to an increase in instantaneous strain within the primary creep regime.

For the PB-SCHT+ aged condition at 140 MPa, the primary creep response for the low porosity specimen is similar to that of the SCHT + aged condition of the parent material. Instantaneous strain is lower for the low porosity bonded condition, and the strain rate decrease is greater for the low porosity bonded condition leading to a lower accumulation of creep strain after 300 hours compared with the parent material in the same SCHT + aged condition. For the PB-SCHT + aged specimen with high levels of centerline porosity, a lower rate of strain rate decrease and higher overall strain level within the primary creep regime occurs even though the instantaneous strain is lower than all other conditions at 140 MPa. The strain rate response of the diffusion brazed

Figure 6.26: Comparison between the parent material in the SCHT condition and the diffusion brazed + PB-SCHT condition at 276 MPa and 760 °C for (a) primary creep, and (b) strain rate versus strain.

(a)

(b)

(c)

Figure 6.27: BSE-SEM images of the diffusion brazed + PB-SCHT specimen subjected to creep conditions of 276 MPa and 760 °C for (a) coarse lamellar colonies and intercolony structure, and (b,c) lamellar structure within the colonies.

(a)

(b)

Figure 6.28: Comparison between the parent material and diffusion brazed conditions at 140 MPa and 760 °C for (a) primary creep, and (b) strain rate versus strain.

condition with high centerline porosity is more indicative of a condition subjected to a higher applied stress level due to pre-existing damage accumulation. The existence of the centerline porosity results in a reduced load bearing cross section and therefore higher effective stress. The higher effective stress results in greater creep strain and creep strain rate within the primary creep regime.

The bonded condition is compared against the parent material condition utilizing a Larson-Miller plot for time to 0.5 % strain and 1.0 % strain (Figure 6.29). LMP values indicate the slight reduction in performance for the diffusion brazed condition in the PB-SCHT condition at 1.0 % strain, while the times to 0.5 % strain are slightly improved in the PB-SCHT condition at 208 MPa and 276 MPa with the exception of the 140 MPa condition. The poor performance at the 140 MPa stress condition is attributed to the high instantaneous strain of approximately 0.5 %. The PB-SCHT + aged condition with high porosity results in lower LMP values than the parent material in the same aged condition, while the diffusion brazed sample with low porosity produces improved LMP parameters and times to 0.5 % strain at a stress level of 140 MPa. Additionally, within the primary creep regime, instantaneous strain is not impacted by the level of defects, however increased size and quantity of pre-existing porosity has a significant impact on the primary transient creep response, and creep rate at 300 hours. These results suggest that at low creep stress (140 MPa) for the aged condition, as long as centerline porosity can be maintained at or below 4 vol%, times to 0.5 % strain that are equal to or greater than the parent material condition are plausible.

(a)

(b)

Figure 6.29: Larson-Miller parameter for the diffusion brazed G2 material alloy at 760 °C and (a) 0.5 % creep strain and, (b) 1.0 % creep strain compared against the G2 parent material condition.

6.3.3 Tertiary Creep & Deformed Microstructures

The creep response of the PB-SCHT condition conducted at 760 °C and 140 MPa, 208 MPa, and 276 MPa is shown in Figure 6.30. As expected, with increasing creep stress, the response exhibit a typical increase in the rate of accumulated creep strain. Also as expected, with increasing creep stress, time to rupture is reduced and occurs at higher rupture strain. Under the high stress conditions of 276 MPa and 760 °C, two diffusion brazed samples in the PB-SCHT condition were evaluated. Both samples exhibit nearly identical primary creep response, however at approximately 45 hours into the the creep test for sample #1, the strain rate significantly increased and the sample ruptured at 47.5 hours and only 1.8% creep strain. A second sample was tested under identical conditions. Interestingly, the instantaneous and primary portion of the creep curve for both samples were remarkably identical. However sample #2 reached an onset of tertiary creep at 1.8 % strain with a minimum strain rate comparable to the unbonded parent material condition (Figure 6.26b). As with sample #1, sample #2 has a shortened tertiary creep regime compared with the parent material response with a rupture time of 104 hours and 2.35 % strain compared with the parent material response of 512 hours and 14.5 % strain (Figure 6.31).

The deformed microstructure near the fracture surface for sample #1 (Figure 6.32) indicates a number of possible mechanisms associated with the short tertiary creep regime of both sample #1 and sample #2. Firstly, as indicated in Figure 6.32, the existence of minor void accumulation (red circles) has occurred within intercolony phases near the fracture surface, while no significant void coalescence appears within the near fully lamellar region adjacent to the brazed zone. This indicates that void initiation and coalescence is confined to the intercolony regions very near the fracture surface (i.e. within the braze zone) and occurs in a relatively short period of time. When a greater volume fraction of intercolony regions exist, void initiation, growth and coalescence is accelerated, reducing overall creep life [157]. This creep acceleration is due to the coarse equiaxed nature of the intercolony grain structure which acts as nucleation sites for voids [52]. This phenomena may partially play a role in the reduced tertiary creep regime due to the reduced volume fraction of lamellar colonies for the PB-SCHT condition, however it would not fully account for the abrupt creep rupture compared with the parent material response under similar conditions.

Figure 6.30: Creep response to rupture for the G2 alloy in the PB-SCHT condition at 760 °C in air with a constant stress of 140 MPa, 208 MPa, and 276 MPa.

Figure 6.31: Creep response comparison to rupture for the G2 alloy in the PB-SCHT condition at 760 °C and 276 MPa (Sample #1 and Sample #2) to that of the parent material in the SCHT condition.

Figure 6.32: BSE-SEM micrograph of the deformed diffusion brazed (PB-SCHT) sample #1 after creep rupture at 276 MPa and 760 °C. Circles indicate areas of void coalescence, while arrows indicate planar fracture regions consistent with pre-existing centerline porosity. Loading direction is vertical with respect to the micrograph.

Secondly, within the intercolony β_0 phase regions, the nucleation and growth of an additional phase has occurred and appears morphologically consistent with the decomposition of the β_0 phase towards an ω phase (Figure 6.33). Since this β_0 phase decomposition was not observed for any parent material condition crept at 760 °C, this β_0 phase decomposition is associated with the diffusion brazing process. The observed decomposition is confined to the braze zone, and is likely a result of a composition variation within the β_0 phase influencing the $\beta_0 \rightarrow \omega_0$ phase transformation temperature ($T_{\omega_0, Solv}$). As found in previous studies [49], decomposition of the β_0 phase for a Ti-43.27Al-4.3Nb-1.17Mo-0.1B (at.%) alloy occurs at temperatures below 825 °C. With decreasing temperature, the ω_0 phase further transforms to ω'' phase at approximately 775 °C. A comparison of beta forming effectiveness between the β_0 phase within the bond zone and parent material prior to creep testing suggest that the significant quantity of Mo and Ni that is partitioned to the β_0 phase due the diffusion brazing thermal cycle acts to further stabilize the β_0 phase. However, it is also postulated in this work that the Ni content potentially has a stabilizing effect on the ω phase in a similar fashion as Nb for high Nb bearing titanium aluminides [49, 158, 159]. Thus, when the braze zone is subjected to an isothermal heat treatment of 760 °C

during creep, the ω_0 and/or ω'' solvus temperatures that have possibly increased due to the presence of Ni, will cause significant nucleation and growth of an ω phase within the β_0 phase. This decomposition was not observed for the parent material under identical creep conditions and is attributed to an optimized quantity of beta stabilizing elements (Nb and Mo) that serve to suppress the decomposition of the beta phase at 760 °C. Based on Figure 6.33, it appears that a considerable volume fraction of the β_0 phase has decomposed in the span of 47.5 hours at 760 °C for the diffusion brazed condition. Within the transformed β_0 phase region, there are bright globular regions interspersed within the primary β_0 phase. Schloffer et al. [49] attributed regions near the β_0/γ interface devoid of the ω phases as regions that transformed to the β_0 phase due to rejection of Mo from the formation of the ω phase. In the β_0 region of the diffusion brazed and crept condition, additional rejection of Ni from the ω phase may lead to a Mo/Ni rich β_0 phase (bright clustering in Figure 6.33b). This phenomena is in contrast to the parent material, where it is postulated that the low combination of Nb and Mo, and a lack of Ni content serve to suppress the ω solvus temperatures below the isothermal creep temperature of 760 °C. A concern with the β_0 phase decomposition to ω is the fact that the ω phases exhibit higher hardness compared to the β_0 phase [49], and thus may contribute to embrittlement of the alloy during creep. However, the unknown effect of Ni additions within the β_0 phase may also influence the ductility of the β_0 phase in either a detrimental or advantageous fashion. Regardless of the impact of the Ni constitution within the decomposed β_0 phase, fracture areas in Figure 6.32 not associated with planar regions generally occur at colony boundaries, and the potential ω phase embrittlement may have played a partial role in the reduced rupture time and tertiary creep regime for the PB-SCHT condition at 276 MPa.

Deformed structures at the fracture interface (yellow arrows in Figure 6.32), reveal a number of elongated planar interfaces that are not associated with fracture at colony boundary or lamellar regions. These planar interfaces are parallel to the braze joint geometry and are likely interfaces associated with pre-existing elongated bondline porosity. Based on Figure 6.32, these planar interfaces account for a significant portion of the fracture interface. It is postulated that the primary factor influencing the short tertiary creep regime and low rupture strain for the PB-SCHT condition at 276 MPa is the pre-existing bondline porosity.

The porosity acts at a minimum to decrease the load bearing cross section of the

(a)

(b)

Figure 6.33: BSE-SEM micrographs of the PB-SCHT condition (Sample #1) after creep rupture near the fracture surface revealing the decomposition of the β_0 phase during creep at 276 MPa and 760 °C. (a) 6.5k magnification (b) 20k magnification,

Figure 6.34: Larson-Miller parameter for rupture time of the the diffusion brazed G2 material alloy compared against the parent material at 760 °C.

sample, and act as crack nucleation sites. Fracture of all specimens was brittle given the low rupture strain with little to no evidence of necking. The low rupture strains are attributed to the pre-existing porosity as well as the minor coalescence of voids within intercolony regions. Evident by the time to rupture LM plot (Figure 6.34), is the difficulty in predicting time to failure for specimens containing different levels of unknown defects. As found in previous studies on cast aluminum alloys [155], with increasing size and quantity of voids, the rupture time is reduced and or unpredictable and may occur within any creep regime (i.e. primary, secondary or tertiary). In this sense, the pre-existing porosity appears to be the main contributor to rupture life since rupture times were somewhat unpredictable between two different sample subjected to the same bonding thermal cycle and creep conditions.

6.3.4 Summary

To establish a baseline for comparison against creep tests conducted on diffusion brazed + PB-SCHT and aged specimens, high temperature creep tests at 760 °C were performed at various constant load initial stress levels ranging from 140 MPa to 276 MPa on the parent material and diffusion brazed in the SCHT and SCHT+aged condition. Findings for the parent material include:

1. During creep, grain growth did not occur for the fully lamellar structures in the unaged and aged conditions. The primary creep resistance of the aged conditions was improved by interfacial $\beta_{0,sec}$ precipitates acting as a barrier to dislocation motion during creep, while creep lives of the aged condition were reduced possibly because of coarsening of intercolony β_0 and γ grains at lamellar colony boundaries, leading to the formation of intergranular voids during tertiary creep.
2. In the unaged condition, fine interfacial $\beta_{0,sec}$ precipitates were formed during creep due to dynamic precipitation resulting in lower minimum creep strain rate than that of the aged conditions. Also, limited growth of equiaxed intercolony β_0 and γ grains at colony boundaries leads to less nucleation of void at the tertiary creep stage resulting in longer creep life compared to the aged condition.
3. It is concluded that controlling the initial microstructure of beta gamma G2 alloy is a key factor if both primary creep and creep life are a concern. Also, it can be suggested that a lamellar structure with continuous α_2 lamellae, and fine interfacial precipitates would be an optimal microstructure for a good balance between primary creep strain and rupture life.

Findings for the diffusion brazed material in the PB-SCHT and/or aged condition include;

1. During creep at low stress, when pre-existing elongated centerline porosity levels are high, primary creep resistance of the aged condition is reduced to levels indicative of the unaged PB-SCHT condition. High pre-existing porosity levels likely contribute to a shortened and unpredictable tertiary creep regime at high stress levels.

2. During creep at high applied stress levels, the PB-SCHT condition exhibits a relatively stable lamellar microstructure with little to no dissolution of α_2 lamellae, and minor dynamic precipitation of interfacial $\beta_{0,sec}$ precipitates at lamellar interfaces that act as a barrier to dislocation motion during creep.
3. During creep at high stress levels, dynamic precipitation of a phase within the intercolony β_0 grains occurred and is consistent with a decomposition reaction whereby β_0 transforms to an ω phase. The decomposition reaction may contribute to void initiation and coalescence within the intercolony regions reducing tertiary creep performance.
4. During creep at low stress levels, when pre-existing porosity levels are maintained below 4 vol.%, primary creep resistance of the aged condition was improved by interfacial $\beta_{0,sec}$ precipitates acting as a barrier to dislocation motion during creep. Compared with the parent material, the PB-SCHT + aged condition exhibited the lowest creep strain rate at a smaller creep strain. Thus, if defects are managed properly, the diffusion brazed condition meets or exceeds the performance of the parent material in the primary creep regime.

Chapter 7

Conclusions and Future Work

7.1 Conclusions

Microstructural and mechanical property evaluation has been conducted for diffusion brazing experiments of a powder metallurgy TiAl-2Nb-2Mo (at.%) beta-gamma Group B alloy bonded with a commercial TiNi67 foil interlayer. Isothermal temperature ranged from 1030 °C to 1150 °C and isothermal solidification times were conducted ranging from 30 minutes to 70 minutes. The following results were found;

1. For diffusion brazing experiments conducted at 1030 °C and 1090 °C, a semi-continuous α_2 structure formed at the solid/liquid interface producing two distinct zones within the braze zone. The central zone consisted of a two phase mixture of β_0 -Ti and a ternary intermetallic phase found to be τ_3 rich in nickel with high hardness as a result of residual liquid cooling. The diffusion zone consisted primarily of $\beta + \alpha_2$ phases with orientation influenced by the lamellar substrate. A nickel rich τ_3 phase was also present in the diffusion zone with a globular or acicular morphology depending on the bonding time and temperature.
2. No γ phase was found within the braze zone for diffusion brazing experiments conducted at 1030 °C. A small quantity of γ phase was found for diffusion brazing experiments conducted at 1090 °C within the diffusion zone which continued to coarsen with increased holding time at 1090 °C.
3. For diffusion brazing experiments conducted at 1150 °C, a semi-continuous layer of disordered α phase formed at the solid/liquid interface enhancing the isothermal solidification rate compared with experiments conducted at 1030 °C and

1090 °C where the ordered α_2 was proposed to have formed at the solid/liquid interface. The enhanced isothermal solidification rate resulted in complete isothermal solidification prior to reaching an isothermal solidification time of 30 minutes. The central zone consisted of no residual liquid on cooling and a high volume fraction of $\beta + \gamma$ phases throughout the bond microstructure along with a finely dispersed Ni rich τ_3 phase.

4. The parent material away from the bondline exhibited lamellar volume fraction reduction to 85-87 vol.%, an increase in coarse lamellar colonies with increasing bonding temperature, increased $\beta_{0,sec}$ precipitation and growth with increasing bonding temperature, and the formation of intracolony globular γ phase at the 1090 °C and 1150 °C bonding temperatures.
5. The growth kinetics associated with each phase within the bondzone were fit to a power law relationship where applicable. The semi-continuous α_2 phase present at all three microstructures exhibited increased microstructural evolution with increasing diffusion brazing temperature. Fitting the measured semi-continuous α_2 layer to a power law relationship reveals that volume diffusion plays a significant role at 1030 °C, while grain boundary diffusion contributed to growth of the α_2 layer at 1090 °C, and eventually grain coarsening became the dominant kinetic mechanism at 1150 °C.
6. Microhardness measurements revealed a marginal decrease in hardness as isothermal holding times increased due to homogenization of the braze zone microstructure. With increased isothermal solidification temperature, hardness levels decreased from a peak of 850 HV for low temperature bonds, to 580 HV for the 1150 °C/70 minute diffusion brazing specimens. The decrease in microhardness at the 1150 °C bonding temperature is attributed to the reduction in volume fraction of Ni rich τ_3 phase as the centerline of the bond, in addition to increased γ phase volume fraction throughout the bondzone.

As-bonded (1150 °C / 70 minute) specimens were taken through a PB-SCHT and PB-SCHT + aging treatment with a goal of forming a fully lamellar microstructure within the braze zone, while re-forming and stabilizing the fully lamellar microstructure of the parent material prior to bonding. For both PB-SCHT and PB-SCHT + aged specimens, the following significant conclusions were drawn;

1. PB-SCHT and PB-SCHT + aged specimens exhibited a graded lamellar volume fraction across the braze zone where the central portion of the braze zone consisted of a fine “near lamellar- β ” microstructure with lamellar colony volume fractions on the order of 75 vol.% within approximately $\pm 300 \mu\text{m}$ of the centerline of the joint.
2. No evidence of the τ_3 phase was found within the microstructure after the PB-SCHT.
3. A graded lamellar colony size ranging from $60 \mu\text{m}$ at the centerline of the braze zone to $90 \mu\text{m}$ in the parent material was realized for both PB-SCHT and PB-SCHT + aged specimens.
4. Upon aging, the intercolony β_0 region within the bond zone exhibited a decomposition reaction whereby the precipitation and growth of two secondary precipitates not previously reported within TiAl diffusion brazed microstructures subjected to post bond heat treatments were found. It is postulated that the bright globular precipitation phase may form via a β phase splitting mechanism, while the identification and formation of the dark platelet phase is inconclusive.
5. Upon aging, both the bond zone and parent material region exhibited the precipitation of an interfacial precipitate within the α_2 lath structure of the lamellar colonies. The bond zone interfacial precipitate is believed to be the β_0 phase which is found to be rich in nickel and experienced significant growth at low aging times. The interfacial precipitate within the parent material is identified as the β_0 phase with expected composition, and exhibited a high density and growth compared with previous studies. The increased interfacial β_0 density within the parent material colonies is attributed to the slower cooling rate from the $T_{F/A}$ temperature compared with air cooling from previous studies.
6. The PB-SCHT condition exhibits a reduction in hardness to 474 HV0.05 compared to the as-bonded condition of 540HV0.05. Further aging resulted in reduced variability in microhardness across the bond zone and a decrease in the average hardness with aging time from 6 hours to 24 hours at 900°C to approximately 415 HV0.05. The reduced variability in hardness across the bond zone

is attributed to a reduction in intercolony hardness as a result of the precipitation of the two unidentified secondary phases. A contribution to the drop in average hardness from the PB-SCHT condition to the 6 hour aged condition is the manifestation of significant interfacial phase precipitation across the entire microstructure.

To establish a baseline for comparison against creep tests conducted on diffusion brazed + PB-SCHT and aged specimens, high temperature creep tests at 760 °C were performed at various constant load initial stress levels ranging from 140 MPa to 276 MPa on the parent material. Diffusion brazed specimens in the SCHT and SCHT+aged condition were subjected to the same creep conditions for a direct comparison of performance associated with the specific Group B beta gamma alloy. Findings for the parent material include;

1. During creep, grain growth did not occur for the fully lamellar structures in the unaged and aged conditions. The primary creep resistance of the aged conditions was improved by interfacial $\beta_{0,sec}$ precipitates acting as a barrier to dislocation motion during creep, while creep lives of the aged condition were reduced possibly because of coarsening of intercolony β_0 and γ grains at lamellar colony boundaries, leading to the formation of intergranular voids during tertiary creep.
2. In the unaged condition, fine interfacial $\beta_{0,sec}$ precipitates were formed during creep due to dynamic precipitation at 276 MPa resulting in lower minimum creep strain rate than that of the aged conditions. Also, limited growth of equiaxed intercolony β_0 and γ grains at colony boundaries leads to less nucleation of void at the tertiary creep stage resulting in longer creep life compared to the aged condition.
3. It is concluded that controlling the initial microstructure of beta gamma G2 alloy is a key factor if both primary creep and creep life are a concern. Also, it can be suggested that a lamellar structure with continuous α_2 lamellae, and fine interfacial precipitates would be an optimal microstructure for a good balance between primary creep strain and rupture life.

Findings for the diffusion brazed material in the PB-SCHT and/or aged condition include;

1. During creep at low stress, when pre-existing elongated centerline porosity levels are high, primary creep resistance of the aged condition is reduced to levels indicative of the unaged PB-SCHT condition. High pre-existing porosity levels likely contribute to a shortened and unpredictable tertiary creep regime at high stress levels.
2. During creep at high applied stress levels, the PB-SCHT condition exhibits a relatively stable lamellar microstructure with little to no dissolution of α_2 lamellae, and minor dynamic precipitation of interfacial $\beta_{0,sec}$ precipitates at lamellar interfaces that act as a barrier to dislocation motion during creep.
3. During creep at high stress levels, dynamic precipitation of a phase within the intercolony β_0 grains occurred and is consistent with a decomposition reaction whereby β_0 transforms to an ω phase. The decomposition reaction may contribute to void initiation and coalescence within the intercolony regions reducing tertiary creep performance.
4. During creep at low stress levels, when pre-existing porosity levels are maintained below 4 vol.%, primary creep resistance of the aged condition was improved by interfacial $\beta_{0,sec}$ precipitates acting as a barrier to dislocation motion during creep. Compared with the parent material, the PB-SCHT + aged condition exhibited the lowest creep strain rate at a smaller creep strain. Thus, if defects are managed properly, the diffusion brazed condition meets or exceeds the performance of the parent material in the primary creep regime.

7.2 Future Work

Dissolution of the parent material plays a crucial role in the kinetics of the overall isothermal solidification process. To better discern the kinetics of the diffusion brazing process for P/M beta gamma alloy, additional isothermal solidification experiments should be attempted to capture the microstructural evolution of the brazed joint at shorter times. Additionally, to better discern the impact of the MPD (nickel) on the resultant microstructure, experiments utilizing a binary TiAl alloy would allow greater accuracy in correlating microstructural evolution of the joint with available ternary phase diagrams.

Limited mechanical testing of beta solidified alloys with small Ni additions have been conducted in the literature. In order to establish the impact of small Ni additions on the bulk properties of the alloy, formulating an alloy that contains a composition consistent with the resultant PB-SCHT braze zone with up to 1 at.% Ni should be generated. From this bulk alloy, the evaluation of both heat treatments and resultant mechanical properties such as creep, tensile, cyclic fatigue, and corrosion testing at room temperature and elevated temperature would allow the impact of the brazing thermal cycle to be discerned from the impact of an additional foreign element within the microstructure.

Given the reduction in lamellar volume fraction associated with the PB-SCHT condition, further heat treatments should be conducted to optimize the lamellar volume fraction within the braze zone, and determine the resultant impact on parent material lamellar volume fraction. Such optimization should be carried out through variation in the PB-SCHT hold temperature, time, as well as optimization of a $T_{F/A}$ temperature for the braze zone composition which is known to be depleted in Al. Alternatively, conducting trials to add Al into the interlayer composition may further minimize the compositional variation between the braze zone and parent material.

Further characterization and identification of a number of phases identified in this work are required. The fine precipitate phases that manifest within intercolony regions during aging of the PB-SCHT condition are required to determine their potential influence on mechanical properties. Further characterization and confirmation of the phase transformations that occur during high temperature creep within the intercolony region of the PB-SCHT condition is of high importance. The decomposition of intercolony β_0 phase, and methods to minimize this effect are required. Further confirmation of the residual liquid transformation on cooling during diffusion brazing should be assessed through TEM evaluation, as well as via a mathematical model of non-equilibrium solidification based on the liquidus projection of the ternary Ti-Al-Ni phase diagram.

Minimization of centerline porosity requires further investigation. The importance of proper jig/fixture design, surface preparation, atmosphere, substrate composition, and bonding pressure likely require optimization to minimize liquid extrusion from the joint.

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Appendix A

Beta Forming Effectiveness Determination

The equivalent beta forming effectiveness in the Ti-Al-Nb-Mo-Ni system is determined as follows. Firstly, the three phase $\alpha_2 + \gamma + \beta$ phase field is determined for each of the Ti-Al-Nb, Ti-Al-Mo, and Ti-Al-Ni systems at constant temperature. Such phase diagram data is available at 1200 °C. The phase-field tie-line transition for each beta forming element versus aluminum concentration is shown in Figure A.1. To determine the equivalent beta forming effectiveness of the system with respect to Mo, the molar ratio at a constant aluminum content is determined where the two-phase $\alpha_2 + \gamma$ region transforms to the $\alpha_2 + \gamma + \beta$ region. An example is shown for a constant concentration of 43 at% aluminum. The molar ratios according to Equation 5.1 are computed for all valid aluminum concentrations. An equivalent beta forming effectiveness with respect to Mo is computed based on Equations 5.2 through 5.4 for each element as shown in Figure 5.3. Since Ni transforms the two-phase region to the three-phase region at lower concentration, it has a greater beta stabilizing effect compared with Mo and further enhances the beta stabilizing effect within the Ti-Al-Nb-Mo system.

Figure A.1: Schematic of the equivalent beta forming effectiveness molar fractions utilized to generate the beta forming equivalency in Figure 5.3