THE UNIVERSITY OF MANITOBA

THE EFFECT OF PROCESSING PARAMETERS ON THE FORMATION OF TITANIUM-TITANIUM ALUMINIDE LAMINATED METAL COMPOSITES

By

DOUGLAS GODA

A thesis submitted to the faculty of Graduate Studies in partial fulfillment of the requirements for the degree of Master of Science

DEPARTMENT OF MECHANICAL AND INDUSTRIAL ENGINEERING WINNIPEG, MANITOBA MARCH 2001



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A Thesis/Practicum submitted to the Faculty of Graduate Studies of The University

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ABSTRACT

In the present investigation, the feasibility of processing a titanium-titanium aluminide laminated metal composite structure has been assessed via two mechanisms of formation: diffusion bonding and self propagating high temperature synthesis (SHS).

Alternating layers of commercial purity aluminum and titanium foils were diffused or reacted at temperatures ranging from 575°C to 640°C to form a layer of titanium aluminide intermetallic. The product material was then evaluated on the basis of morphology and chemistry using SEM, EDS, and X-ray diffraction techniques. Specific emphasis was placed on the degree of consolidation of the aluminide, phase chemistry, and quality of the metal-intermetallic bond.

Subsequent examination showed that despite the mechanism of formation (diffusion bonding or SHS), the resulting aluminide layer was composed completely of TiAl₃. This was confirmed by both EDS and X-ray diffraction analysis, where the presence of other stable equilibrium phases (Ti₃Al and TiAl) was not detected.

It was observed in diffusion bonding experiments that formation of titanium aluminide began with the initiation of an SHS reaction at the interface of the elemental metal foils via the grain boundaries. Following this, reaction proceeded by normal diffusion mechanisms, obeying a typical parabolic growth rate with respect to annealing time, yielding a consolidated, homogeneous layer. SHS reactions were found to result in a drastically different morphology than that observed in diffusion bonding experiments. Specimens were characterized by a band of spheroidal particles, composing a loosely consolidated layer at the titanium-aluminum foil interface. Diameter of the particles averaged 1-5 μ m, with total layer thickness of approximately 10 μ m.

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Chapter 1

INTRODUCTION

1.1 Composite Materials and Laminated Metal Structures

As an engineering material, structural composites have enjoyed a rich history, which extends as far back as two to three thousand years to ancient Chinese and Egyptian civilizations, where straw was used as a reinforcing component in clay or mud used to build homes and fortifications. Even then, however crude the level of understanding, people knew of the advantages of composite structures.

Laminated metal structures, in contrast, are a relatively new concept to material science, almost completely unexplored prior to the 1960's. Now, with current emphasis in the aerospace industry of providing new materials that are lighter, stronger, and resistant to exposure at higher temperatures, LMCs are gaining unparalleled popularity as a potential replacement material in modern aircraft and spacecraft.

1.2 Titanium Aluminides

Titanium aluminides encompass a group of intermetallics created by the alloying of titanium and aluminum. They are recognized in the metallurgical community as materials which posses superior high temperature properties and oxidation resistance while maintaining low density [1]. However, titanium aluminides are plagued by low

ductility and fracture toughness [2], and thus their application as commercial alloys is hindered. Nonetheless, research efforts focused on improving their ductility have made advances, therefore the future of the intermetallics as a commercially viable material seems much more promising.

Like most other intermetallics, titanium aluminides first gained popularity in the 1950's, which, with the advent of plastics and other non-metallic materials, waned through the 1970's and early 1980's. In the mid to late 1980's, aluminides re-emerged and interest in them was restored, with focus on applications in the aerospace industry as a replacement material in gas turbines. Presently, it is speculated that titanium aluminides, and various other titanium-based alloys will form the components used in some of the highest temperature areas of next generation of jet engines.

1.3 Objective: Titanium-Titanium Aluminide Laminated Metal Composites

It is the brittle nature of titanium aluminide that restricts its use without either alloying or incorporation into a composite structural material. More recently, it is the latter approach which has been the focus of some investigation. By combining the low density, high strength properties of titanium aluminide, with the superior toughness characteristics of titanium, a composite structure endowed with each of these properties may be realized, while retaining the favorable high temperature properties of each. This has been the underlying objective of the present research project to gain insight into the processing parameters and techniques that will give rise to just such a material.

There are a number of processing techniques available to accomplish such a feat, from cold roll bonding to chemical reaction and diffusion bonding [2,3]. In this work, the techniques of diffusion bonding and Self-propagating High- temperature Synthesis (SHS) were investigated.

In each case, the starting materials were pure titanium and aluminum foils, stacked in an alternating sequence to form a sandwich-type structure. The aluminide formed by diffusion or SHS reaction between the foils to produce a layer of intermetallic. It is the growth rate of this layer, its morphology, and chemistry, as well as influences of various processing parameters on these properties, which form the basis of this study.

Chapter 2

LITERATURE REVIEW

2.1 Phase Equilibria and Thermodynamic Properties

2.1.1 The Titanium-Aluminum Phase Diagram

The phase diagram for titanium and aluminum has undergone a number of revisions since it's initial proposal in 1951 by Ogden [4]. Some of the more notable changes were proposed by Bumps [5] in 1952, Schubert [5,6] in 1964, and Murray [7] in 1988 (Figure 2.1). Presently, the most widely accepted diagram is that in Figure 2.2, taken from Petzow and Effenberg [8]. The controversy of compositional limits and transformation temperatures still exists, especially in the higher temperature ranges of the phase diagram. However, for the purposes of this work, the diagram proposed Murray shown in Figure 2.1 has been used. This diagram was selected as it differentiates α -TiAl₃ as an individual phase rather than grouping it with higher temperature TiAl₃, which has a distinctly different structure.

2.1.2 Thermodynamic Data

Thermodynamic values for intermetallics of the titanium-aluminum system are quite sparse. The limited data available, are credited to the work of Kubaschewski and Dench [9], and Kubaschewski and Heymer [10], where values of heat of formation were derived through direct reaction calorimetry. Entropy values for TiAl and TiAl₃ were derived by Samakhvol et al [11, 12]. Barin, Knake, and Kubaschewski [13] are the sole source of published heat capacity values of titzanium aluminides.



Figure 2.1: Titanium-aluminum phase diagram proposed by Murray. [14]



Figure 2.2: Titanium-aluminum phase diagram published by Petzow and Effenberg. [8]

•

2.1.3 Summary of Titanium-Aluminum Structures

α Titanium:

 α -Titanium has a hexagonal A3 structure (Mg-prototype), with lattice parameters of c = 0.468 nm and a = 0.295 nm [15]. α -Titanium occurs in the Ti-Al system over a composition range of 51.5 to 100 at.% Ti, and transforms in the most pure state at a temperature of 882°C to β -titanium [14]. Typically, α -titanium is utilized in the aerospace industry in alloyed form for castings. It is a material renowned for its oxidation resistance and toughness.

β Titanium:

Pure β -titanium possesses a cubic A2 (W-prototype) structure, with a lattice parameter a= 0.331 nm [15]. β -titanium occupies a slightly broader compositional range than α -titanium, spanning 55 to 100 at.% Ti at 1490°C, and has a melting point of 1670°C at 100 at.% Ti [14].

α_2 -Phase (Ti₃Al):

One of the two most widely recognized aluminide phases, Ti_3Al exists as an ordered hexagonal $D0_{19}$ structure (Ni₃Sn – prototype), with lattice parameters a = 0.5780 nm and c = 0.4647 nm [15]. The compositional range of stability Ti₃Al is from 22 to 36 at.% Al at 600°C [14]. Kubaschewski [11] places a value of ~ -26.369 kcal/mole for the heat of formation of Ti₃Al, which is not a widely published figure. This corresponds to a free energy of formation value of approximately -26.3 kcal/mole (see Appendix A). Ti₃Al, due to its high strength at elevated temperatures, is a perfect candidate for application in gas turbines [16]. However due to its low ductility, it has seen little application. When alloyed with manganese, Ti₃Al, has shown some improvement in ductility [16].

γ-Phase (TiAl):

 γ -titanium aluminide crystallizes with a tetragonal L1₀ structure (AuCu-prototype) with lattice parameters a = 0.400 nm and c = 0.408 nm [15]. Its range of composition covers 48 to 60 at.% Al, and has a melting point of 1460°C at a composition of 52.5 at.% Al [14]. The free energy of formation of TiAl is ~ -16.9 kcal/mole, and the heat of formation is ~ -17.4 kcal/mole. TiAl, much like Ti₃Al, is receiving a great deal of attention from the aerospace industry due to its low density-high strength characteristics. However, it too suffers from low ductility, and because of this has also seen little commercial application.

TiAl₂:

TiAl₂ is a phase that has two structural variations, a lower temperature orthorhombic phase with lattice parameters a = 0.403 nm and c = 0.396 nm (Ga₂Zr – prototype), and a higher temperature phase with tetragonal structure with lattice parameters a = 0.3976nm

and c = 2.436nm (Ga₂Hf – prototype) [15]. The lower temperature structure is commonly referred to as the α TiAl₂ phase, which is present on the phase diagram proposed by Murray [14] at a single composition of 66 at.% Al. The temperature at which it transforms to TiAl₂ remains in question, although it is speculated to be approximately 780°C [14]. The higher temperature phase is commonly grouped with the Ti₂Al₅ and Ti₅Al₁₁ (referred to as ξ -titanium aluminides [8]) which occupy compositional limits of 65 to 68 at.% Al at 1387°C.

TiAl₃:

TiAl₃ is quite similar to TiAl₂ in that it has two structural variations, a lower temperature tetragonal variant based on a superstructure of the D0₂₂ lattice, and a higher temperature tetragonal D0₂₂ structure [15]. Lattice parameters of the two are a = 0.3875 nm, c = 3.384 nm and a = 0.385 nm, c = 0.858 nm [15] respectively. To distinguish between the two, the low temperature variant is commonly referred to as α TiAl₃ [17].

The earliest documentation of the α -TiAl₃ phase was by van Loo and Rieck [17], who observed formation of the structure at temperatures below 600°C. X-ray diffraction showed the lattice of the material to differ substantially from that of ordinary TiAl₃ which formed at temperatures above 600°C. They found that subsequent annealing of the lower temperature phase above 600°C would not induce transformation. Similar behavior was observed when annealing TiAl₃ at temperatures below 600°C.

As one of the most thermodynamically stable of the titanium-aluminum intermetallics, TiAl₃ has a heat of formation (ΔH_f) of ~ -34 kcal/mole, and a free energy of formation of ~ -32.5 kcal/mol [11].

ξ-Titanium Aluminides (TiAl₂, Ti₅Al₁₁, Ti₂Al₅):

The region of the phase diagram (Figure 2.2) in which these compounds lie is poorly understood. The exact location of compositional range and melting points of each phase remains unknown. Best estimates place the compositional limits of these three phases somewhere within 65 to 73 at.%Al at 1387°C. It is understood that each possesses a tetragonal structure with the following lattice parameters [15]:

Ti_5Al_{11}	a = 0.392 nm	c = 1.653 nm
Ti2Al5	a = 0.390 nm	c = 2.92 nm
TiAl ₂	a = 0.3976 nm	c = 2.436 nm

To date, there have been no thermodynamic data generated for these phases Table 2.1 summarizes the properties of the various titanium aluminide phases.

Phase	Unit Cell	Crystal Structure	Compositional Limits	Transformation, Temperature	ΔHf	ΔG
α-Ti		Tetragonal, A3 c=0.468nm a=0.295nm	48.5 to 0 %at. Al	α.→β at 100 %at. Ti 882°C	_	
β-Τί		Cubic, A2 c=0.331nm	45 to 0 %at. Al at 1490°C	β→L 100 %at. Ti 1670°C		_
Ti₃Al		Hexagonal, DO ₁₉ c=0.465nm a=0.578nm	22 to 36 %at. Al at 600°C	Ti ₃ Al → α Ti ~32 %at. Al at ~1180°C	~-26.369 kcal/mol	~-26300 cal/mol
TiAl		Tetragonal, $L1_0$ c=0.408nm a=0.400nm	48 to 60 %at. Al at 1120°C	TiAl → L(Ti, Al) ~56 %at.Al at ~1460°C	~ -17.4 kcal/mol	~-16920 kcal/mol
αTiAl₂		Ortho- rhombic c=0.396nm a=0.403nm	66 %at. Al	αTiAl ₂ →TiAl ₂ ~66 %at. Al at ~780°C	_	
αTiAl₃		Tetragonal c=3.384nm a=0.388nm	75 %at. Al	αTiAl ₃ →TiAl ₃ ~75 %at. Al at ~600°C	~ -34.0 kcal/mol	~-32503 kcal/mol

Table 2.1: Crystal structures, composition limits, transformation temperatures,

and thermodynamic data for titanium aluminide intermetallic phases [7, 11, 14, 15, 17].

2.2 Physical Properties and Mechanical Behavior of Laminated Metal Structures

As a relatively new development to the field of composite science, laminated metal composites or LMCs, are a class of materials capable of demonstrating a broad array of characteristics. Through careful selection of starting materials, properties such as high strength, low density, and superior fracture characteristics may be achieved. The individual traits that an LMC exhibits are derived from the parent materials of which it is composed. Utilizing this as a design principle, it becomes possible to fabricate materials for very specific and demanding environments.

The degree to which an LMC demonstrates any one specific trait is governed by the rule of mixtures [18], which suggests that a composite structure will inherit a specific attribute based on the volume fraction of the contributing material. Therefore, by controlling the ratio of the materials that form the composite, one can control the properties of the end product. However, prediction of all physical properties is not so simple. The rule of mixtures can be quite accurate for approximating bulk physical properties such as thermal conductivity and density. However, it fails to address the material on a microstructural level, where variations exist [19]. Moreover, it assumes ideal bonding between the constituent phases, which makes it very inaccurate when attempting to estimate properties such as elastic and shear modulii [19]. Hence, quantification of mechanical properties of the composite structure must be done by experimental methods. An alternating laminar structure can be quite advantageous when considering the mechanical properties of an LMC [20]. Careful selection of materials from which a composite is formed can provide it with an inherent crack-arresting structure [21]. A crack arresting structure (Figure 2.3) is one in which crack propagation is halted by placing an intermediate material of higher fracture toughness perpendicular to the path of cracking [21]. Research performed by Cook and Gordon [22] showed that in the case where interfacial bond strength between two successive lamina was lower than that of the arresting material, a crack would preferentially follow the interface between the materials, in effect, controlling the direction of crack propagation. Assuming that the bond between the adjacent materials is stronger than that of the fracturing medium, crack propagation could also be prevented. By effectively utilizing a crack-arresting structure, it becomes possible to control fracture characteristics and mode of failure of a structure [21].

2.3 Processing Techniques for Production of LMCs

There are a number of viable processing techniques available for the production of LMCs on a commercial scale. These can be divided into four major categories: deformation bonding, diffusion bonding, electro-deposition, and combustion synthesis [3, 23, 24]. Of these, deformation bonding and diffusion bonding have seen the largest degree of industrial implementation, whereas combustion synthesis and electro-deposition have yet to realize their potential as manufacturing processes. For the purposes of brevity, only diffusion bonding and combustion synthesis techniques will be discussed.



Figure 2.3: Typical arrangement of a crack-arresting structure.

Diffusion bonding, as it is applied to the formation of LMCs, involves the transport of atoms across an interface of two adjacent lamina, to facilitate a sound metallic bond between them. Rate of the process is regulated by four variables: time, temperature, pressure, and surface quality of the mating materials [25, 26]. The role of first two variables, time and temperature, is deeply rooted in the theory on which diffusion is based. These are the rate controlling variables. With an increase in either, thickness of the bonding diffusion layer will increase as per the equation:

$$\Delta x^2 = k D_0 e^{-Q/RT} \bullet \Delta t \tag{1}$$

Where: Δx is the thickness of the diffusion layer
Q is activation energy in Joules/mole
T is temperature in Kelvin
D_o is a pre-exponential term, independent of temperature
Δt is the diffusion annealing time in hours.

Pressure and surface quality of the material, although not accounted for in the diffusion equations, can have a profound effect on the rate of diffusion, as well as the quality of bond. Pressure is used to ensure intimacy of contact between the diffusing species, and to cause deformation of surface asperities that prevent good surface contact [26]. Surface properties may affect the quality of bond between two materials by altering the rate at which they diffuse. As well, the presence of oxide scales on the surface of the materials may prohibit diffusion, or limit the amount of surface penetration of the diffusing atoms [17].

Combustion synthesis refers to the initiation of an exothermic chemical reaction between two or more materials which possess a large enthalpy difference between products and reactant [24]. As applied to the formation of an LMC, combustion synthesis can be used to form a composite structure by reaction between two successive lamina [27]. Depending on the chemistry of the phase formed, reaction may result in the formation of brittle intermetallic, compromising bond strength.

One of the earliest uses of combustion synthesis was the thermite process. Conceived at the latter part of the 1800's, the technique was used as a welding process for railway track [28]. By packing a mixture of aluminum and iron oxide powder at the joint of two pieces of rail, an exothermic reaction was initiated by the addition of a small amount of heat (relative to the melting point of the two materials). This type of reaction forms the basis of much more recent adaptation of combustion synthesis.

Self-propagating High-temperature Synthesis (SHS) uses the exothermic heat of formation of a compound in order to create a self-sufficient reaction [28], which propagates across the interface of two reacting species. Applied to the formation of a composite structure, it can be used to create a reaction layer between two materials to bond them. If it is allowed to go to completion, an SHS reaction can be used to produce a composite composed of parent material, and a reaction product [27].

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As a processing technique, SHS reactions find their roots in the field of powder metallurgy, where powdered reactants are mixed, compacted, and a reaction initiated to form a compound or mixture of compounds. Application of SHS to bulk materials such as foils or slabs has been somewhat limited. However, with an increased understanding of reaction kinetics, SHS certainly has the potential to become a process practiced on a commercial scale.

2.4 Formation of Titanium-Titanium Aluminide LMCs via Diffusion Bonding

A great deal of research has been dedicated to the study of diffusion in the titaniumaluminum system. However, it is important to point out that little has been done in applying this knowledge to the formation of titanium-titanium aluminide LMCs. When compiled, the available diffusion data provides a wealth of information directly applicable to the production of LMCs, and gives some insight into the processing requirements of them.

2.4.1 Relative Mobilities

Of primary interest, is the inter-diffusivity of the two elements. There seems to be some inconsistency here, as there are two very opposing viewpoints on the subject. Based on a series of marker experiments, van Loo and Rieck [17] suggested that it was aluminum which diffused more readily into titanium. By placing 10 μ m molybdenum wires or zirconium oxide powder at the interface of the two materials, they observed the presence of aluminum on both sides of the marker. This, they reasoned, was caused by the movement of aluminum around it, demonstrating that it possessed a much higher diffusivity than titanium.

Rao and Houska [29], who studied sputtered aluminum films on a titanium substrate concurred, but acknowledged the higher mobility as ".. the release of aluminum into α -titanium".

In complete contrast are the two works of Luo and Acoff [30, 31]. Conducting a series of experiments with high purity aluminum and titanium foils at temperatures of 660°C and 680°C [30], as well as 900°C and 1200°C [31], they observed the "...expansion of aluminum rich layers" at the apparent expense of thinning titanium layers, as well as the movement of the titanium-titanium aluminide interface towards titanium. They considered this to be caused by the movement of titanium atoms into the aluminum layer, and concluded that the net flux of atoms across the interface was much higher for titanium. Some SEM micrographs were provided which they suggested corroborated this.

Work done by Fukutomi et al [32] regarding void formation in aluminum during diffusion, apparently took neither side in the discussion of relative mobility. However, their thoughts on diffusion of aluminum and titanium through the intermetallic phase, TiAl₃, were certainly intriguing. According to their model, upon formation of the intermetallic layer, titanium is restricted to diffusion within TiAl₃, implying that it was not free to diffuse through and into aluminum. Aluminum, on the other hand, was free to diffuse into both. They based this argument on the solubilities of the two materials. From the binary Ti-Al phase diagram, it is observed that pure α -titanium is capable of forming solid solutions over a broad compositional range, from pure α -titanium, up to 51.5% at. Al at approximately 1460°C. Aluminum, however, forms almost no solid solutions in titanium. Thus they suggested that titanium diffused only into the intermetallic.

It becomes apparent from just these few references, that although there is some disagreement on which is the more rapidly diffusing element, the consensus appears to favor a model in which aluminum is considered to be the more mobile species. This of course assumes a vacancy-based mode of lattice diffusion, ruling out any possible grain boundary contributions.

2.4.2 Diffusion Mechanisms: A Grain Boundary Alternative?

Diffusion between materials can be facilitated by two major mechanisms: vacancy diffusion and grain boundary diffusion. Depending on the diffusing species, one or more of these mechanisms may contribute to the transfer of mass across the Ti-TiAl₃-Al interfaces. In the previous section, the direction of diffusion between titanium and aluminum was described as the predominant movement of aluminum into titanium. This assumed that a vacancy mechanism was responsible for mass transfer. Under certain conditions however, some believe that a contribution of grain boundary diffusion may influence rates, and, even the direction of diffusion.

In a paper on diffusion of sputtered titanium films on large grained aluminum substrates, Zhao, Nicolet and Thulliard [33] discuss the concept of transition metal transfer via grain boundary diffusion in polycrystalline aluminum. They reference this from previous work
by Zhao and Nicolet [34] who performed similar work with nickel and aluminum. These authors found that in small-grained aluminum, the abundance of grain boundaries would facilitate diffusion of nickel through them. In their work with titanium and aluminum, they state that the presence of lateral non-conformities (i.e. non-planar interfaces), could be explained by the contribution of grain boundary diffusion, although this was dismissed as an active mechanism.

Revisiting the work of van Loo and Rieck [17], it is found that they too discussed the possibility of grain boundary diffusion. Performing theoretical calculations of activation energy and frequency factor for diffusion of aluminum in titanium aluminides, they found the values to be rather low when compared to the rapid diffusion behavior they observed in their couples. The model on which their calculations were based assumed an ordinary vacancy mechanism. The discrepancy between the two, they concluded, could be due to a possible grain boundary diffusion of aluminum through titanium aluminide. As an alternative to this, they suggested a model where rapid vacancy diffusion could have occurred, but dismissed this on the basis that it required an unusually high vacancy concentration in the aluminum sub-lattice of the aluminide layer.

2.4.3 Chemistry of the Resultant Layer

When producing a layered composite by diffusion bonding, the chemistry of the resulting phases is of particular interest. Thermodynamics dictates that one should expect to see some manifestation of each of the phases stable at the equilibrium temperature. This

however is not the case for the formation of intermetallics. The formation of a phase can be heavily influenced by growth kinetics of the phase, as well as by its ability to nucleate. In the diffusion of titanium and aluminum, it has been observed that in almost every case the TiAl₃ phase is the first to nucleate [17, 29, 30, 31, 32, 33], and is the phase which forms in the greatest abundance at temperatures below the melting point of aluminum.

Kidson and Miller [35] were probably one of the first to publish their observations of this phenomenon. Although their work was centered on interdiffusion of zirconium and aluminum, the results are equally applicable to titanium-aluminum couples due to a number of similarities that these systems share. They found that on diffusing high purity zirconium and aluminum couples, ZrAl₃ was the only phase to form. Microprobe analysis of the intermetallic layer showed that whereas zirconium concentration remained relatively constant throughout the reaction layer, there existed a slight concentration gradient for aluminum (Figure 2.4). It was suggested that this was caused by an increase in the number of un-occupied sites in the aluminum sub lattice of the ZrAl₃ layer. They surmised that in the presence of such a gradient, that aluminum would diffuse much more rapidly, such that it "... swamps the formation and growth of any of the expected intervening phases.".

Experimental work in another paper published by van Loo and Rieck [36], suggests that the absence of other phases is a problem of kinetics, not nucleation. In an experiment, TiAl₃ and titanium were bonded (samples were actually furnished by previous work [17]), and annealed at 800°C. Upon examination of the specimen, they observed the presence



Figure 2.4: Concentration gradient in ZrAl₃ layer observed by Kidson and Miller [35].

of all of the aluminide phases (Ti_3Al , TiAl, and $TiAl_2$). This, they claimed, precluded the inability of these phases to nucleate. It was also stated that although the presence of these phases was not detected in titanium-aluminum couples, that they must be present in some immeasurably small form.

The works of Luo and Acoff [30], and Rao and Houska [29] are in agreement with the results of van Loo and Rieck. However it should be noted that they did not observe the formation of a $TiAl_2$ layer on subsequent annealing of $TiAl_3$ and titanium. Both also observed the rate of growth of other titanium rich phases to be quite slow relative to that of $TiAl_3$.

2.4.4 Growth Rate of the Intermetallic Layer

Upon nucleation of the intermetallic phase across the titanium-aluminum interface, layer growth begins. According to normal diffusive behavior, Fick's relationships are followed:

$$J = -D \bullet \Delta C / \Delta x \quad (2)$$

where:

J is the atomic flux

D is the diffusivity constant

 ΔC is the concentration gradient, or change in composition

 Δx is the distance of atomic movement, or distance traveled by an atom

The relationships predict growth to follow a parabolic time dependence, which is generally described as thickness varying as a function of time^{1/2}. Deviation from this behavior can occur in some instances, but only in the case where concentration gradient and interdiffusion coefficient are not constant.

In those experiments where growth rate has been measured, diffusion of titanium and aluminum appears to follow a typical thickness-time parabolic relationship [17]. When found to be otherwise, the presence of oxide scales on the titanium surface was usually thought to be the cause [17, 35], and it was observed that once the layer had been penetrated, normal parabolic growth resumed.

2.4.5 Layer Morphology

The intermetallic layer resulting from solid-state diffusion of titanium and aluminum is usually found to be uniform in thickness with a high degree of homogeneity (Figure 2.5).

In most cases (with only a few minor exceptions [17]) the layer is found to be non porous and nearly parallel to the original interface [30]. Specimens annealed above the melting point of aluminum tend not to show the high degree of consolidation typical of those processed in the solid state, as evidenced when comparing the micrographs presented in Luo and Acoff's [31] work done at 600°C and 900°C (Figure 2.6).

Contrary to most reports, Kidson et al [35], and van Loo and Rieck [17], did observe porosity in the intermetallic layer (Figure 2.7). Both derived rather rudimentary explanations as to the cause of this porosity, including the saturation and breakdown of oxide scales on solid solution particles of aluminum found in the intermetallic layer [17], and a large-scale Kirkendall effect [35].



Figure 2.5: Typical TiAl₃ intermetallic layer produced by diffusion of titanium and aluminum diffusion annealed at 635°C, 40 minutes. [37]



(a)



(b)

Figure 2.6: Samples prepared at (a) 600°C and (b) 900 °C, 4 hours. [31]



Figure 2.7: ZrAl₃ layer produced by diffusion bonding of zirconium and aluminum foils with the presence of voids both internally and at the aluminum zirconium interface. [35]

2.5 Combustion Synthesis Reactions

Combustion synthesis can be described as the formation of a compound by means of an exothermic chemical reaction, initiated at some temperature sufficiently below the melting point of the compound. Reactant materials are usually in the form of powders that are pressed into a green compact, however, combustion synthesis may be applied to foils or slabs, where it has been used as a bonding technique [38, 39]. The reaction can occur via two modes, simultaneous combustion (thermal explosion), or self-propagating mode. The self-propagating mode is generally prescribed the acronym SHS for Self-propagating High-temperature Synthesis.

The two modes of combustion are characterized by a significant difference in reaction initiation and kinetics. The simultaneous combustion reaction requires heating reactants to the point of ignition, where reaction occurs at all interfaces of the two or more reactant species. This requires uniform heating throughout the entire specimen, and is generally performed in a vacuum furnace. Conversely, SHS requires that the reaction be initiated only at a point, where the high heat of formation of product material provides sufficient heat to allow the reaction to propagate throughout the specimen. On a practical level, it is accepted that most combustion synthesis reactions are a mixture of both modes of formation. The reaction kinetics of each combustion mode is illustrated in Figure 2.8.



Figure 2.8: Reaction kinetics of combustion synthesis and SHS reactions.

The heat generated by the combustion synthesis reaction is caused by large enthalpy differences between product and reactant materials [40]; hence, the reaction can only be initiated between materials that form compounds with large negative free energies of formation. As a rule, it has been claimed that SHS reactions can not be initiated and sustained by materials which fail to achieve a combustion temperature of 1800K [41], however, there are exceptions to this, as these reactions have been found to initiate and propagate to completion at significantly lower temperatures [42, 43].

To understand the fundamentals of combustion synthesis reactions, it is prudent to first identify four significant temperatures which influence and can profoundly affect the mode of reaction [24], reaction kinetics, and ultimately the product of reaction. The adiabatic temperature, (Tad), is defined as the theoretical temperature achieved at the reaction site, and is the maximum possible temperature which can be achieved by the exothermic formation of product material. This assumes that no heat loss to the environment or surrounding material occurs. Combustion temperature (T_c), is the actual temperature of the reaction, taking into account heat loss to the surrounding material/environment and non-ideality of the combustion process. The ignition temperature, (Tig), is the temperature required to cause the exothermic reaction to initiate between reactants. Finally, the initial temperature of the reactants, (T_0) , is the temperature of the material immediately prior to ignition. In the case of simultaneous combustion, this temperature corresponds to the ignition temperature, (Tig). For SHS reactions, T₀ is considered the temperature prior to reaction initiation, or at a distance

sufficiently far from the initiation site such that the temperature of the reactants has not been elevated by the reaction.

The relationship of the temperatures described above defines the type of reaction (simultaneous combustion or SHS) that occurs between the reactant species [43]. In the combustion synthesis reaction, the initiation temperature and initial temperatures coincide, such that:

$$T_0 = T_{ig} \qquad (3)$$

This situation is created by preheating the reactant materials. Because each potential reaction site is heated to its ignition point, exothermic reactions initiate throughout the specimen. Unlike the SHS mode, in simultaneous combustion reactions, heat is not required to cause initiation at other points in the sample; therefore, none of the heat produced at each reaction site is absorbed by neighboring material and all heat generated by the specimen must either go into the formation of product or be rejected to its surroundings. If all heat generated by reaction is absorbed by the reaction, the following relationship between combustion and adiabatic temperatures results:

$$T_c \rightarrow T_{ad}$$
 (4)

and all available heat is used in the formation of product. This situation is, however, highly unlikely as it requires a completely adiabatic process. It is important to note

however, that the heat evolved from a simultaneous combustion reaction is significantly higher than that of an SHS reaction.

The temperature relationships of an SHS reaction differ somewhat from the simultaneous combustion scenario as each temperature (T_0 , T_{ig} , T_c , and T_{ad}) has a unique value. The relationships between them more closely approximates the following:

$$T_0 \leq T_{ig} \leq T_c \leq T_{ad} \qquad (5)$$

This implies that the material (at its initial temperature T_0) is raised to its ignition temperature, T_{ig} , at a point on its surface by a source such as the localized application of heat, or a reaction in surrounding material. This initiates an exothermic reaction at the interface of the reactant species. Temperature at the reaction site is elevated to the combustion temperature T_c , which is lower than that theoretically attainable (T_{ad}) due to heat dissipation to the surrounding material. It is this evolution of heat which raises the temperature at adjacent reaction sites to the ignition temperature, causing reaction, and further propagation of the reaction in the form of a wave front.

The temperature relationships for both the simultaneous combustion and SHS reactions, and their relative magnitudes, are illustrated in Figure 2.9.



Figure 2.9: Temperature relationships of simultaneous combustion and SHS reactions.

2.6 Formation of Titanium Aluminides via Combustion Synthesis Reactions

Considered to be one of the more attractive future processing techniques [44], combustion synthesis reactions are an appealing alternative to conventional casting. This is due to the relatively low energy requirement of the process, where the melting of titanium is not required, and the numerous complications associated with casting of the intermetallic alleviated.

The overwhelming majority of research efforts centered on the combustion synthesis of titanium aluminides have concentrated on reactions between powdered materials. From this research, relationships between particle size, processing pressures, heating rates, and their effect on resulting microstructure and chemistry have been derived and studied extensively. Work with foil reactants has also been performed, although not to the same extent as that of powders. Compilation of available data for reactions of both media yields rather interesting similarities, including reaction initiation and combustion temperatures as well as compositional control techniques and resulting chemistry.

2.6.1 Reaction Initiation Temperature

Generally, it is accepted that the initiation of reaction between titanium and aluminum, in both powder and foil forms, occurs at a temperature coinciding with the melting point of aluminum (~660°C). This has been evidenced by experimental work involving direct measurement [27, 45], differential scanning calorimetry (DSC) [39] and differential thermal analysis (DTA) [46]. In each case, immediately following the endothermic trough associated with the liquidus of aluminum, an exothermic event of significant magnitude was observed which elevated the temperature of the specimen. A typical temperature profile illustrating the effect is shown in Figure 2.10. Preceding this reaction, at temperatures between 520°C to 620°C, a small exothermic peak was also observed (Figure 2.11). The combustion temperature of this reaction was approximately 600°C to 650°C, which appeared to decrease with increased heating rate. At heating rates less than 2 K min⁻¹, no initial exothermic reactions were observed. It is thought that the origin of these pre-cursory peaks can be explained by the formation of titanium oxides [46].

In contrast, some believe that the ignition temperature of the titanium-aluminum reaction lies below the liquidus of aluminum, suggesting a solid-state reaction. Work performed on SHS reactions in powder compacts suggests that ignition occurs at temperatures ranging between 550°C to 600°C [47], with the exact temperature of ignition depending on size of the powder particles. Reduction in particle size appeared to result in a reduction of ignition temperature.

2.6.2 Combustion Temperature

Measured combustion temperatures may vary with mode of formation (simultaneous combustion or SHS), form of the reactant materials (powder or foil) and the phases formed by reaction, as well as a number of experimental variables including placement of



Figure 2.10: Increase in specimen temperature observed to coincide with the initiation of a combustion synthesis reaction between titanium and aluminum. [48]



Figure 2.11: Initial exothermic peak observed in titanium-aluminum specimens during heating to the ignition temperature.

thermocouple, size and thermal conductivity of die or heating platens. Hence, measurement of T_c is very subjective and easily influenced.

Combustion temperatures measured in powder compact specimens reacted by simultaneous combustion, range between 1100° C to 1400° C [47, 49] for mixtures of 50%at.Al - 50%at.Tā (corresponding to a stoichiometric ratio for TiAl). At the upper limit of this range, the reaction temperature begins to approach the adiabatic temperature for formation of TiAl (1460° C [49]) by simultaneous combustion. Combustion temperatures of 1175° C to 1275° C [49] have been measured in powder mixtures corresponding to stoichiometric ratios of TiAl₃. This is marginally lower than the published adiabatic temperature of 1340° C [49] for simultaneous combustion reactions.

In specimens reacted by SHS, combustion temperatures for stoichiometric powder mixtures of TiAl₃ are approximately ~1200°C [50]. This value is particularly high, approaching the adiabatic temperature for the formation of the compound (T_{ad} TiAl₃ =1244°C) [49]) for this type of reaction.

Measurement of combustion temperature in foil specimens becomes a more complex problem than in powder specimens. Placement of thermocouples at the reaction interface is difficult at best, and is intrusive as its presence can influence the reaction itself. Thus, accurate measurements of combustion temperature have yet to be made. As the only readily available reference, the plot shown in Figure 2.12 demonstrates a timetemperature profile for an SHS reaction.

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Figure 2.12: Temperature-time profiles at 3 locations on a specimen surface for foil sample reacted via SHS. [50]

2.6.3 Powder Mixtures, Foil Thickness and Resulting Aluminide Chemistry

The ability to control composition of resulting phases is of singular importance when forming titanium aluminides by combustion synthesis reactions. Techniques have evolved for both powder and foil reactants to accomplish this, both of which have met with mixed success.

In powdered specimens, the convention of mixing reactants in stoichiometric ratios has become common practice when attempting to achieve a specific phase. This technique has only been successful for specific processing parameters and additional heat treatment employed. In the work of Moore and Petric [49], it was observed when mixing ratios of 50 % at. Al – 50% at. Ti, that the desired TiAl phase was formed only when the compact was heated at a rate greater than 50 K min⁻¹. At rates below this threshold value the presence of other phases, specifically Ti₃Al and TiAl₃, was observed.

Uenishi et al [39] obtained similar results when attempting to produce Ti_3Al by mixing stoichiometric ratios of titanium and aluminum, and heating compacts at a rate of 20 K min⁻¹. The predominant formation of TiAl₃ phase was observed, along with trace quantities of TiAl and residual titanium. The material was eventually homogenized to a composition of Ti_3Al and TiAl only after heat treatment at temperatures in excess of 1500K for prolonged periods.

Paransky et al [47], in their work on reactive synthesis of TiAl from stoichiometric powder blends, observed that full conversion of the powder compact to γ -phase could not be realized. In specimens rapidly heated to 700°C, phases including TiAl, Ti₃Al, TiAl₂ and pure titanium were detected in the specimen by X-ray diffraction. Those rapidly heated to 900°C yielded a mixture of 60% TiAl – 40% Ti₃Al at the center of the specimen, with trace quantities of TiAl₂ at its periphery. They concluded that the higher temperature was responsible for furthering the conversion of reactants to TiAl. It was also suggested that in samples heated to 700°C, conversion was prevented by heat loss to surrounding material from the combustion zone.

Comparing the work above to available thermochemical data, it becomes apparent that unless threshold processing parameters are observed, the formation of intermetallic phases is governed almost exclusively by free energy of formation.

Compositional control in samples prepared from foils is more complex than from powder reactants. This is due to the inability to intersperse the reactant species in fixed quantities. Yet, if control of resulting chemistry is fundamentally governed by reactant availability, then varying foil thickness is one approach to attaining it. This technique has been practiced [51, 52], however, it too has met with limited success.

The work of Jacob and Speidel [52] with hot isostatically pressed titanium and aluminum foils, showed that desired compositions could be obtained, but only after subsequent heat treatment. They observed that by reaction annealing at temperatures below the liquidus

of aluminum, $TiAl_3$ formed readily at the interface of the two foils. Small quantities of Ti_3Al and TiAl were also found in limited quantities. Heat treatment at 1300°C for approximately 1 hour successfully transformed the materials to the desired TiAl phase.

The principal formation of TiAl₃ as observed by Jacob and Speidel is common to many other works including that of Alman et al [27, 45], Rawers [53, 54] and others [55]. In almost all cases where processing was carried out at temperatures above 660° C or heat treated at similar temperatures, a fine band of TiAl was observed to accompany the predominant TiAl₃ layer.

2.7 Scope of the Present Investigation

In the preceding introduction and literature review, it was shown that as a prospective aerospace material, titanium-titanium aluminide LMCs have the potential to offer a wide variety of attractive features including high specific strength, excellent high temperature properties, and unique fracture characteristics. However, it was also demonstrated that understanding of the two most viable techniques for processing such a material is limited, and fraught with inconsistency. Nonetheless, there is one underlying commonality to all of the works discussed, which shows that the morphological and chemical result of diffusion/SHS of titanium and aluminum, is a function of processing parameters and their manipulation.

The focus of the present investigation was to facilitate a deeper understanding of the effect of processing parameters on the mechanisms of formation of a titanium aluminide layer from titanium and aluminum foils. The effects of these variables on two processing techniques, diffusion bonding and self-propagating high-temperature synthesis, were examined. In diffused specimens, annealing temperature, annealing time and foil thickness were altered to provide evidence of their influence on growth rate of the intermetallic layer. SHS experiments were conducted over a range of heating rates to demonstrate their possible effect on reaction initiation and combustion temperatures. Common to both, was examination of how each of the variables described above influence the morphology and chemistry of the resultant aluminide layer. From this, models for the effect of processing parameters on the mechanisms responsible for aluminide formation in diffusion bonded and SHS reacted specimens were proposed.

Chapter 3

EXPERIMENTAL PROCEDURE

3.1 Materials

In an effort to avoid ambiguity of results due to impurities, commercially pure metals were selected for the construction of all samples.

3.1.1 Titanium

99.9% commercial purity titanium foil, provided by Bristol Aerospace Ltd., 0.002" thick was selected for sample construction. The foil was cut into $\frac{34}{7}$ " x $\frac{34}{7}$ " squares and lightly sanded with 600-grit silicon carbide paper to remove rough edges caused by cutting. 0.015" thick titanium sheet, of similar composition, was also used, and prepared in a similar manner.

3.1.2 Aluminum

Aluminum foil donated by Alcan Canada Ltd., 99.999% pure, 0.004" and 0.0045" thick was the second metal used in sample construction. As required, the material was chemically milled to furnish 0.002" and 0.001" thick foils necessary for diffusion bonding experiments. The material was used in the as-received condition. To ensure purity, independent chemical analysis was performed on the foils by mass spectrometry.

3.2 Specimen Preparation

The following describes the procedures used in the preparation of specimens for SHS and diffusion bonding experiments.

3.2.1 Chemical Milling of Aluminum Foils

As required in the diffusion bonding experiments, 0.001" and 0.002" thick aluminum foils were produced by chemical milling of 0.004" aluminum foils. A TEA or Tri-Ethyl-Amine solution was prepared consisting of:

43 ml Tri-Ethyl-Amine
132 g Sodium Hydroxide
25 g Sodium Sulfide
~1 L Distilled Water

and heated to its boiling point (approximately 90°C). $\frac{3}{4}$ " x 6" strips of 0.004" thick aluminum foils were immersed in the solution, and surface material was removed. The foil strips were periodically taken from the solution, rinsed with distilled water and measured with a micrometer. They were then re-immersed and the procedure repeated until desired thickness was attained. When completed, the foils were soaked in distilled water to ensure that material removal had ceased.

3.2.2 Rolling and Annealing of Aluminum Foils

In the latter stages of experimental work, it became necessary to produce 0.004" thick foils from 0.0045" aluminum, due to shortage and unavailability of 0.004" material. This was accomplished by cold rolling of 0.0045" foil in three passes, until a uniform thickness of 0.004" was achieved. The material was then annealed at 410°C for a period of one hour to restore grain size.

3.2.3 Etching and Cleaning of Foil Surfaces

Due to the rapid formation and tenacity of the oxide scale which formed on both the titanium and aluminum foil surfaces, it was necessary to clean the materials by chemical etching. Although this process did not completely remove the scale, it controls the thickness of the layer, yielding more reproducible results from diffusion bonding and SHS processing.

³/₄" thick squares of titanium foil were etched using a modified Krolls reagent, consisting of:

54 parts Distilled Water
40 parts Nitric Acid (HNO₃)
6 parts Hydrofluoric Acid (HF)

These were immersed in the etchant for a period of 30 seconds, or until the straw colored tarnish was removed from the foil surface (maximum of 45 seconds). The material was then rinsed with distilled water, de-smutted using a mixture of 50% distilled water-50% nitric acid, and rinsed once again in boiling distilled water. Cleaning was completed by wiping the foil with lint-free tissues, and storing in vacuum ($1x10^{-3}$ Torr) until used.

Aluminum foils were prepared by chemical etching in a 20% sodium hydroxide solution for 30 seconds, then rinsing in distilled water. The $\frac{3}{4}$ " squares were then dried with a lint-free wipe, and stored in vacuum (1x10⁻³ Torr) until used.

It is important to note that both titanium and aluminum foils were handled with tweezers throughout the cleaning and sample preparation process. Oils secreted by skin readily deposit themselves on the surfaces of the foils, impeding or preventing diffusion or SHS reactions between the materials. Therefore, cleanliness was imperative to the success of the experiments.

3.3 Sample Assembly and Packaging

Samples were constructed from layers of titanium (0.002") and aluminum (0.001", 0.002", 0.004" and 0.0045") foils, stacked in an alternating sequence between two 0.015" thick titanium end plates as per the illustration in Figure 3.1. The assembly was then wrapped in titanium foil and spot welded along its periphery to prevent pre-processing oxidation, and to act as an oxygen getter during annealing. A completed sample assembly is shown in Figure 3.2.



Figure 3.1: Stacking sequence of titanium and aluminum foils.



Figure 3.2: Assembled sample in titanium foil wrapping.

3.4 Sample Storage

Due to the affinity of aluminum and titanium for oxygen, it was necessary to store samples under vacuum of at least 1×10^{-3} Torr to prevent oxidation prior to processing. It was found that samples could be stored under such conditions for up to 24 hours without significant detrimental effects on diffusivity or chemical reactivity of the metals.

3.5 Diffusion Bonding

Specimens prepared from 0.001", 0.002", and 0.004" thick aluminum foils were taken from evacuated storage, and placed in a static loading compression device (Figure 3.3). Directly adjacent to the sample, a type K thermocouple was placed to facilitate temperature measurement. The device was loaded into a 2" bore vacuum chamber (Figure 3.4), and suspended vertically in a static load frame, with a weight pan attached. The specimen was then pre-loaded to 35.5 psi. A SpeediVac vacuum system equipped with mechanical and diffusion pumps was used to evacuate the vacuum chamber to approximately 1x10⁻⁵ Torr, after flushing with commercial purity argon. The complete experimental apparatus is pictured in Figure 3.5.

Once high vacuum was established, a split furnace was clamped around the vacuum chamber, and the sample heated at a rate of 9 to 14 °C/min to processing temperatures of 575°C, 595°C, 615°C and 635°C. Upon reaching the processing temperature, stress on the sample was increased to 125 psi. Specimens were subsequently annealed for times

ranging form less than 1 minute to 360 minutes. After annealing, samples were cooled by removing the furnace from the vacuum chamber.

3.6 SHS Reactions

Due to the rapid heating requirements of the SHS experiments, a Gleeble 1500 thermomechanical simulator was used as the processing apparatus. The Gleeble 1500 (Figure 3.6) is an extremely versatile and powerful research tool as it allows for the application of tensile or compressive load, while providing rapid electrical resistance heating in an evacuated or inert gas purged environment.

For this series of experiments, two 316 stainless steel anvils, $\frac{3}{4}$ " in diameter, were fabricated and placed in the hydraulic rams of the Gleeble (Figure 3.7). Samples were placed between the anvils with a 0.010" chromel alumel thermocouple attached to its edge. The purpose of the thermocouple is to provide temperature feedback to the automated control system of the Gleeble. An additional thermocouple was attached to the specimen, and connected to a National Instruments data acquisition system, to provide additional temperature measurement. The Gleeble specimen chamber was then evacuated to 1×10^{-3} Torr with a mechanical vacuum pump.



Figure 3.3: Static loading compression device.



Figure 3.4: Vacuum chamber.



Figure 3.5: Experimental apparatus: Diffusion bonding experiments.


Figure 3.6: Gleeble 1500 thermo-mechanical simulator.



Figure 3.7: Anvil and sample arrangement in the Gleeble 1500.



Figure 3.8: Thermal cycle of a sample reacted at 100°C/minute.

Samples were hydraulically loaded to 70 lbs., or 125 psi, through the stainless steel anvils, and heated to 300°C at a rate of 20°C/minute, where temperature was allowed to homogenize for 5 minutes, then ramped to 640°C at heating rates of 6.25, 12.5, 25, 50, 75, and 100°C/minute. Temperature was maintained for a period of one minute, after which specimens were cooled at a rate 20 °C/minute to 350°C then allowed to cool in air. Figure 3.8 illustrates a typical heating cycle for a sample reacted at 100°C/minute.

3.7 Sectioning, Mounting and Polishing of Specimens

Due to the brittle nature of titanium aluminides, specimens were sectioned using an Agema-Spark EDM machine. In this manner, shattering of the aluminide layer by abrasive cutting could be avoided. Specimens were cut across the mid-section, assuming that this region would be representative of the morphology and chemistry of the bulk material. After sectioning, samples were mounted in either black Bakelite resin or clear epoxy resin in 1 ¼" dies.

Preparation for metallographic analysis began by mechanical polishing on 120, 240, 400 and 600 grit silicon carbide sandpapers. A finishing polish using 6 μ m, 1 μ m, and ¹/₄ μ m diamond pastes and colloidal silica slurry provided an appropriate finish for SEM analysis.

Specimens which were examined along the planar direction of aluminide layer formation were sectioned by EDM, and split along the aluminum-titanium aluminide interface by cooling with liquid nitrogen and shearing with a thin blade and hammer. Samples were subsequently analyzed in un-mounted form. Figure 3.9 shows the arrangement of planar and transverse sections used in analysis.



Figure 3.9: Transverse (a) and planar (b) sections of samples as prepared for examination.

3.8 Scanning Electron Microscopy and EDS Chemical Analysis

Metallographic analysis was conducted on JEOL 840, JEOL 5900, and Phillips XL30 scanning electron microscopes (Figure 3.10). Examination was conducted at accelerating voltages of 12 to 20 kV, which was set as required in both secondary electron and back-scattered electron imaging modes. Working distances used ranged from 39 to 10 mm depending on the required field of view. All analyses were conducted in high-vacuum mode.

Semi-quantitative EDS analysis was performed on the JEOL 5900 scanning electron microscope which was equipped with an Oxford EDS detector and analysis system, using INCA standardless correction software. Atomic compositions were generally obtained with accelerating voltage fixed at 20kV and a working distance of approximately 15mm with a dead time of 40%, which were considered optimal acquisition conditions for the system. Point, area and line scans were used to quantitatively ascertain atomic composition of the aluminide phases formed, while phase mapping was used for examination of element dispersion.

A typical EDS point scan is shown in Figure 3.11.



Figure 3.10: (a) JEOL 840, (b) JEOL 5900 and (c) Phillips XL-30 Scanning electron microscopes.



Figure 3.11: Typical EDS point scan provided by JEOL 5900 scanning electron microscope and Oxford EDS system.

3.9 X-Ray Diffraction

To positively identify the phases present in diffusion and SHS reacted specimens, a Rigaku D/MAX-2000 X-ray diffractometer (Figure 3.12) was used to generate X-ray patterns. These patterns were cross referenced with available powder diffraction files included in the JADE XRD analysis package, and identification was made of all compounds present in the samples. Specimens were affixed to a glass slide which provided an amorphous background, simplifying the process of peak identification. Slides were mounted in a standard aluminum specimen holder and placed in the diffractometer unit for analysis. Figure 3.13 is a typical spectrum acquired from the system for TiAl₃, Ti, and Al.



Figure 3.12: Rigaku D/MAX-2000 X-ray diffractometer.



Figure 3.13: Typical X-ray spectra obtained from the Rigaku X-ray diffractometer.

Chapter 4

RESULTS

4.1 Diffusion Bonding

4.1.1 Morphology of the Aluminide Layer

Specimens Processed at 635°C

Metallographic examination of specimens processed by annealing at 635°C revealed that the aluminide layer which had formed at the titanium-aluminum interface was both homogeneous and highly consolidated. Fine bands of porosity, noted both in previous work [37], and by others [17,35], was absent in all specimens. The results of SEM secondary and backscattered electron imaging suggested that the layer formed was composed of a single aluminide phase, where no significant contrast difference was observed within the intermetallic layer. Figure 4.1 is a typical micrograph taken of a sample prepared from 0.004" thick aluminum foils.

Collection and examination of micrographs taken of each specimen for the entire range of annealing times, yielded interesting trends in the uniformity of the aluminide layer formed for each foil thickness. It was observed that layers became increasingly regular (i.e. planar) with increased foil thickness. This is demonstrated in Figure 4.2, for specimens prepared from 0.001", 0.002", and 0.004" aluminum foils which have been annealed for 30 minutes. The validity of this relationship was observed in several similar micrograph sets for each annealing time.



100 µm

Figure 4.1: Transverse section of specimen diffusion bonded at 635°C, 40 minutes, constructed from 0.004" aluminum foils (Mag. 330X).



(c)

Figure 4.2: Transverse sections of specimens annealed at 635°C for 30 minutes constructed from (a) 0.001" Al foil (*Mag. 650X*), (b) 0.002" Al foil (*Mag. 430X*), and (c) 0.004" Al foil (*Mag. 270X*).

Growth of the aluminide layer was characterized by notable decrease in the thickness of aluminum foil. As annealing times increased, available aluminum rapidly decreased along with a less remarkable decrease in titanium layer thickness. Eventually, all available aluminum was consumed, leaving a titanium aluminide layer bonded to a titanium substrate (Figure 4.3). Duration of anneals leading to this microstructure for each foil thickness are provided in Table 4.1.

Demonstrating the brittle nature of titanium aluminides, some specimens exhibited cracking in the intermetallic layer, parallel to the direction of layer growth. Figure 4.4 is a micrograph of a specimen formed from 0.004" aluminum foils, annealed for 50 minutes. Cracks tended to manifest themselves at random, and were at first thought to be caused by thermally induced stresses due to cooling from the annealing temperature. A series of additional experiments where cooling rate was altered dispelled this assumption, as it was found that cracking could not be induced reliably. Therefore, the cause of cracking could not be ascertained experimentally.



100 µm

Figure 4.3: Transverse section of sample annealed at 635°C for 6 hours, constructed from 0.004" Al foils. (Mag 230X).

Thickness (inches)	Annealing Time (minutes at 635°C)
0.001	~ 60
0.002	~ 120
0.004	~ 240

Table 4.1: Duration of anneals required for the consumption of aluminum for 0.001",0.002" and 0.004" aluminum foils.



100 µm

Figure 4.4: Transverse section of specimen annealed at 635°C, 50 minutes, constructed from 0.004" Al foils. (Mag 270X)

Specimens Processed at 575°C, 595°C, and 615°C

Specimens which were diffusion annealed at 575°C, 595°C, and 615°C produced significantly thinner titanium aluminide layers for a given annealing time as compared to those annealed at 635°C, demonstrating a definite dependence on temperature. This is of course the behavior predicted by the Fick equations, and is illustrated in Figure 4.5 which is a plot of layer thickness versus diffusing temperature for 4 different annealing times. Here, the exponential effect of temperature on thickness of the diffusion zone is clearly verified.

Imaging the fine intermetallic layers produced in samples at these lower processing temperatures proved to be quite difficult in cross-sectioned specimens. The layers that formed appeared consolidated and homogeneous (Figure 4.6), however, concerns raised about poor image quality led to the planar sectioning of specimens to confirm their morphology. This revealed that the structure of the layers was quite different than anticipated. Layers formed in samples annealed at 575°C from 40 to 360 minutes were found to be composed of loosely agglomerated globules (Figure 4.7), with diameters processed at temperatures up to 595°C for annealing times approaching 4 hours. Beyond this point, aluminide layers appeared to become increasingly consolidated, with aluminide particles eventually blending to form a solid layer. The relationship between morphology, annealing time and temperature is illustrated in Figure 4.8.



Figure 4.5: Aluminide layer thickness versus annealing temperature.



Figure 4.6: Transverse section of specimen annealed at 575°C for 6 hours. (Mag. 23000X)



Figure 4.7: Planar section of sample annealed at 575°C, 360 minutes. (Mag. 200X)



Figure 4.8: Relationship between annealing time and temperature with specimen morphology.

Due to the uneven fracture surface created by splitting the samples along the aluminide layer, a unique opportunity to study the interface of the titanium-titanium aluminide layers presented itself. Here, the presence of titanium aluminide at the grain boundaries of the titanium foil was observed (Figure 4.9), and was found to maintain a globular morphology as seen in the bulk layer. This suggested that grain boundaries were primary nucleation sites for the aluminides.

4.1.2 Chemistry of the Aluminide Layer

Specimens Processed at 635°C

Preliminary semi-quantitative EDS analysis of the aluminide layer showed that the intermetallic consisted of 25% at. Ti, 75% at. Al, which is a perfect stoichiometric match for the TiAl₃ phase. A representative spectrum of a specimen, annealed for 50 minutes, is provided in Figure 4.10. In addition to point analyses, line scans were also performed, showing that the composition across the aluminide layer remained constant (Figure 4.11).

To confirm the results of EDS analysis, X-ray diffraction was performed on specimens produced from 0.004" thick aluminum foils. Samples annealed for 2, 8, 30, and 50 minutes were sectioned across the aluminum-titanium aluminide interface and examined. Results of the analysis showed that the phase formed in each specimen was indeed TiAl₃, with a $D0_{22}$ crystal structure identifying it as the higher temperature variant of TiAl₃ which forms at temperatures above 600°C. A typical XRD spectrum for a sample annealed for 50 minutes is provided in Figure 4.12.



Figure 4.9: Titanium aluminide found nucleated at the grain boundaries of pure titanium in planar sectioned specimen annealed at 595°C, 40 minutes. (Mag 800X)



Figure 4.10: Typical EDS spectrum produced by point analysis of aluminide layer found in specimen annealed at 635°C, 50 minutes.



Figure 4.11: Typical line scan produced by analysis of aluminide layer found in specimen annealed at 635°C, 50 minutes.



Figure 4.12: Typical XRD spectrum for a sample annealed at 635°C, 50 minutes.

Specimens Processed at 575, 595, and 615°C

As a preliminary approach to identifying the aluminide phase formed in these specimens, EDS analysis was conducted on transversely sectioned specimens. Point and line scans performed across the aluminide layer indicated a composition of TiAl₃. However, due to the small quantity of material formed ($<5\mu$ m thick), the accuracy off the analysis was questionable. For this reason, the specimens were split along the pelane of aluminide formation and analyzed by X-ray diffraction.

Diffraction analysis showed that the aluminide layer formed in almost call specimens was composed completely of TiAl₃. Further examination also revealed that the crystal structure of the aluminide was $D0_{22}$, a variant structure of the TiAl₃ phease found to form at temperatures above 600°C. A typical X-ray spectrum is shown in Figure 4.13.

One notable exception to the near exclusive formation of TiAl₃, weas observed in a specimen annealed at 615°C for 4 hours. X-ray diffraction identified the composition of the aluminide layer as Ti_2Al_5 , a non-equilibrium high temperature phase spanning a compositional range of 70 to 72% at., at temperatures above 1200°C. A_n X-ray spectrum for this specimen is shown in Figure 4.14.



Figure 4.13: XRD spectrum typical of samples showing TiAl₃ composition (annealed 595°C, 6 hours).



Figure 4.14: XRD spectrum for a sample annealed at 615° C, 4 hours, showing Ti₂Al₅ composition.

4.1.3 Growth Rate

From measurements of aluminide layer thickness in specimens for each annealing time/temperature combination, it was observed that layer thickness demonstrated definite parabolic time dependence. This is illustrated in Figure 4.15, where layer thickness versus annealing time is plotted for 0.004" Al samples diffused at 575°C, 595°C, 615°C, and 635°C. Also demonstrated by the plot, is the marked decrease in aluminide layer growth with decreased annealing temperature.

Figure 4.16 shows another plot of aluminide layer thickness versus annealing time for specimens processed at 635°C, constructed from 0.001", 0.002" and 0.004" foils. It is apparent from the plot that the parabolic growth relationship holds, however, it is also important to note that growth rate is significantly lowered with decreasing foil thickness in these experiments.



(a)



(b)

Figure 4.15: Thickness versus time plot of specimens annealed at 575°C, 595°C, 615°C, and 635°C.



Figure 4.16: Plot of aluminide layer thickness versus annealing time for specimens processed at 635°C, constructed from 0.001", 0.002" and 0.004" foils.

4.2 SHS Reactions

4.2.1 Reaction Kinetics

From temperature measurements taken during heating, it was observed that in all specimens, regardless of the heating rate, exothermic reactions occurred. Figure 4.17 is a plot of temperature versus time for a typical specimen heated at a rate of 100 °C/minute, showing the sharp rise in temperature associated with the initiation of an SHS reaction. From similar plots constructed for each heating rate (6.25, 12.5, 35, 50, 75 and 100°C/minute), several notable observations were made.

A distinct drop in ignition temperature of the exothermic reaction was observed to occur at heating rates above 25°C/minute. In the plot shown in Figure 4.18, it can be seen that reactions initiated at rates below 25°C (i.e. those conducted at 12.5°C and 6.25°C), ignition temperature ranges from 590°C to 595°C. At heating rates above 25°C/min, initiation of the reaction occurs at temperatures ranging from 550°C to 570°C. This is in reasonable agreement with the work of others [1, 53], which suggest initiation of the reaction while both metals are in the solid state.

Also observed, was the occasional occurrence of small pre-cursory reactions, such as those seen in Figure 4.19, for heating rates of 100, 50 and 6.25 °C/minute. These reactions, which were marked by small exothermic peaks, tended to occur at temperatures


Figure 4.17: Typical thermal profile of a specimen processed at 100°C/minute.



Figure 4.18: Thermal profiles of specimens prepared at 6.25, 12.5, 25, 50, 75 and 100°C/minute.



Figure 4.19: Plots of temperature versus time for samples prepared at 100, 50 and 6.25°C/minute indicating the presence of a pre-cursory exothermic event of limited magnitude.

ranging from 515°C to 580°C.

Plots of temperature versus time for various heating rates also suggest a distinct dependence of measured reaction temperature on heating rate. Again referring to Figure 4.18, it is apparent that there is a well-defined decrease in the magnitude of heat evolved during the reaction in specimens heated at rates lower than 25 °C/minute. Table 4.2 outlines the difference in temperature rise of specimens for each of the six heating rates sampled. From the table, it is clear that between heating rates of 25°C/minute to 12.5 °C/minute, there is a significant change in the heat evolved by the combustion synthesis reaction.

4.2.2 Morphology of the Aluminide Layer

Examination of specimens by SEM in both secondary electron and back-scattered mode, revealed that the morphology of the aluminide layer in SHS reacted specimens is quite different than that observed in those formed by diffusion bonding. The aluminide produced via SHS consisted of a collection of loosely consolidated globules, approximately 1 to 5 μ m in diameter (Figure 4.20, sample heated at 100°C/minute), forming a layer roughly 5 μ m thick. Figure 4.21, which is a specimen heated at 100°C/minute, demonstrates the morphology typical of that formed in most specimens. Globules of different diameters were randomly distributed.

Heating Rate (°C/minute)	Temperature Rise (°C)
6.25	~8
12.5	~8
25	~50
50	~37
75	~39
100	~50
100 ~50	

Table 4.2: Temperature rise recorded in specimens produced by SHS reaction and the corresponding heating rate at which the specimen was heated.

A collective examination of all specimens produced at the various heating rates showed that little variation existed between them. Apparently heating rate had no influence on the resulting morphology of the aluminide layer. This can be seen in Figure 4.22, where micrographs of specimens heated at 6.25°C/minute and 100°C/minute respectively are compared. The only significant variation in morphology was the presence of residual aluminum between the aluminide layers (Figure 4.23), which was thought to be caused by an inability to extrude it from the sample packaging. This in turn was caused by the absence of discontinuities in the spot weld at the package periphery.

Thickness of the aluminide layer varied little from sample to sample. The layer formed at each titanium-aluminum interface was almost a constant 5μ m, independent of heating rate. It was also observed that degree of consolidation of the globules did not change with heating rate, thus as a rule, heating rate had little effect on the general morphology of the SHS reacted specimens.

4.2.3 Chemistry of the Aluminide Layer

Preliminary chemical analysis of the titanium aluminide layer formed in SHS reacted specimens, was conducted by EDS. The results of thorough examination suggested that in every specimen, TiAl₃ was the only phase formed, with analysis showing a near



Figure 4.20: Globules observed to form in samples produced by SHS reaction by heating at 100°C/min (planar section). (Mag. 900X).



Figure 4.21: Typical morphology of the aluminide layer produced by SHS reaction (heated at 100°C/minute, transverse section), of titanium and aluminum foils (Mag. 3500X).



(a)



Figure 4.22: Transverse sections of specimens prepared at (a) 6.25°C/minute (Mag. 750X) and (b) 100°C/minute (Mag 1500X) demonstrating little difference in morphology.

perfect stoichiometric atomic ratio of 25 at% Ti-75 at% Al. A typical EDS spectrum demonstrating this is provided in Figure 4.24. Due to the small size of the aluminide particles composing the layer, it was necessary to perform X-ray diffraction on some specimens to ensure the accuracy of phase identification. This would also provide valuable information on the crystal structure of the aluminide layer.

X-ray diffraction corroborated the EDS analysis in identifying the composition of aluminide phase as TiAl₃. Examination of the PDF file from which this composition was matched, showed that the phase possessed a DO_{22} structure, corresponding to the higher temperature variant of TiAl₃. This was significant, as it showed that formation of the phase occurred at a temperature above 600°C, thus verifying the exothermic nature of the reaction. A typical X-ray spectrum of a specimen processed at a heating rate of 6.25°C/minute is provided in Figure 4.25.



Figure 4.23: Residual aluminum layer found to occasionally remain in specimens (transverse section). (Mag.850X).



Figure 4.24: Typical EDS spectrum of specimens produced by SHS reaction.



Figure 4.25: Typical X-ray diffraction spectrum of an SHS reacted specimen. Pictured is a spectra taken from a sample prepared at 6.25°C/minute.

Chapter 5

DISCUSSION

5.1 Diffusion Bonding

The resultant chemistry and morphology of the aluminide layer produced in diffusion bonding specimens suggests that there is a more complex mechanism responsible for layer growth than simple binary diffusion. The presence of high temperature phases, stable only beyond the annealing temperature and the globular nature of the aluminide substantiate this. When compared to the results of the SHS work, it would appear that the mechanism which lead to the observed characteristics of the diffusion bonded specimens is indeed the same as for SHS. The following is a proposed model for the formation of titanium aluminide in the diffusion bonded specimens.

The process of layer growth presumably begins with the diffusion of aluminum into titanium. The results of marker experiments conducted by Van Loo and Rieck [17] suggest that this is the predominant direction of mass transfer. This is a logical assumption considering the high mobility of aluminum at the annealing temperature which is proximal to the melting point. Diffusion of aluminum would continue to the point of saturation, where instability would cause the initiation of an exothermic combustion synthesis reaction, resulting in the formation of an initial layer of titanium aluminide of a few microns in thickness. The presence of this layer has been observed, and was evidenced in a number of SEM micrographs for samples annealed at short durations (i.e. less than 2 minutes at 635°C, less than 20 minutes at 575°C).

It is quite likely that grain boundaries act as primary initiation site for the reaction which forms the initial layer. Because grain boundaries are recognized as high energy areas, the activation energy requirements to initiate the reaction would be lower than that within the grain. Thus, nucleation of the aluminide phase would occur first at the grain boundaries. This was confirmed in SEM micrographs and phase maps of planar sectioned specimens, where the presence of aluminide was observed only at the grain boundary, with the rest of the grain left unaffected.

Due to the formation of the initial layer, further growth of titanium aluminide is limited to the rate at which reactant material can be supplied to a reaction site. This requires either titanium, aluminum, or both to diffuse through the intermetallic layer, hence rate of layer growth becomes diffusion controlled. This was evidenced by the plot shown in Figure 5.1, in which a best-fit curve was ascribed to the data points generated from thickness versus time measurements of 0.004" aluminum samples annealed at 635° C. The equation assigned to the curve (of the form y=Ax^B), showed an exponent term equal to 0.42. For an ideal diffusion controlled process, thickness of the diffusion zone is roughly proportional to the square of time, thus, for an ideal plot of thickness versus annealing time, the exponent term should be equal to 0.5. The derived value of 0.42 is in good agreement with the theoretically ideal value when possible sources of experimental error are considered.



Figure 5.1 Thickness versus time plot of 0.004" aluminum specimens annealed at 635°C.

Aluminum, due to its higher mobility, is the most likely to diffuse through the intermetallic and further the growth of the titanium aluminide layer. A high vacancy concentration in the aluminum sub-lattice of the TiAl₃ layer, or possible grain boundary diffusion of aluminum through TiAl₃ (as proposed by Van Loo and Rieck [17]), may expedite the process of mass transfer through the intermetallic layer.

Once aluminum atoms have penetrated the aluminide layer, the process of diffusion into titanium to the point of saturation, and subsequent reaction to form titanium aluminide repeats itself. This mechanism will continue until the complete consumption of all available aluminum occurs.

The proposed model of aluminide layer growth is shown schematically in Figure 5.2.

Evidence for a combustion synthesis-based mode of aluminide formation comes from Xray analysis of the resultant aluminide layer. Analysis of the crystal structure of all but one diffusion bonded specimen, regardless of annealing temperature, showed that the phase belonged to a higher temperature (above 600°C) variant of TiAl₃ possessing a D0₂₂ structure. This structure would be impossible to achieve in specimens annealed 575°C and 595°C unless some form of exothermic reaction had occurred to increase the temperature above 600°C.

The combustion temperature achieved by the exothermic reaction in the diffusion bonded specimens during the formation of the initial layer, is presumed to be quite high,



Figure 5.2: Schematic model of aluminide formation in diffusion bonded specimens.



Figure 5.2(cont'd): Schematic model of aluminide formation in diffusion bonded specimens.

approaching the adiabatic temperature for formation of TiAl₃ (~1340°C). The presence of Ti₂Al₅ in specimens annealed at 615°C confirms this assumption. Unstable at temperatures below 1200°C, the phase could not possibly have formed unless the magnitude of the exothermic event had reached a minimum of 1200°C. It is quite likely that the high temperature phase was retained when cooling from the combustion temperature due to a quenching effect caused by unusually rapid cooling rates subsequent to its formation.

The simplified model proposed above may now be amended to include details of phase transformation in the intermetallic phase. Immediately following initiation of the combustion synthesis reaction, TiAl₃ is formed at the reaction site. This is associated with the evolution of a large quantity of heat, which raises the temperature of the newly formed intermetallic to the temperature of transformation to Ti_2Al_5 . Rapid heat dissipation on completion of combustion to neighboring regions causes reversion to the lower temperature TiAl₃ phase, with a crystal structure of DO₂₂. The inability of TiAl₃ to transform to α TiAl₃ at temperatures below 600 °C, forces the aluminide to retain its higher temperature DO₂₂ structure.

The resulting microstructure of the titanium aluminide layer, showing increased degree of consolidation with increased annealing time and temperature, is certainly curious and comparable to that of the SHS reactions. The globular morphology observed would seemingly suggest formation of intermetallic in the liquid state. Globules or spheroids are a morphology generally associated with solidification of materials, where the rounded

structure of particles corresponds to a reduction of surface energy upon transformation to the solid state. This scenario is however impossible in the formation of the TiAl₃ phase. The adiabatic temperature for formation of TiAl₃ is approximately 1340°C [49]. This is the maximum achievable temperature that can be obtained by combustion synthesis reaction under ideal conditions. When compared to the melting point of TiAl₃ of 1387°C [14], it becomes clear that melting or formation of the phase in the liquid state is simply not possible. Therefore, the globular morphology of the layers must be attributed to a mechanism of the reaction rather than the temperature of combustion.

Degree of consolidation of the aluminide layer, which demonstrated a definite dependence on annealing temperature and time, must be a function of interdiffusion between the aluminide globules. At elevated annealing temperature, or, after prolonged annealing times, interdiffusion between the aluminide globules would have a coalescing effect, where the individual particles would appear to blend together. The end result of this would be a homogeneous mass, showing a high degree of consolidation much like that observed in specimens annealed at 635°C for a period of several hours. The time/temperature dependence of consolidation is derived from directly from the effect of these variables on rate of interdiffusion, where an increase in each results in a proportional increase in interdiffusion, thus expediting homogenization of the layer.

Differences of aluminide layer growth rate observed in specimens constructed from 0.001", 0.002", and 0.004" aluminum foils could be attributed to a variation in surface quality of the foils prior to annealing. Since thinner foils (0.001" and 0.002") were

produced by chemical milling of thicker (0.004") material, surface quality was degraded resulting in a coarser pitted surface. With the increased appearance of surface asperities created by chemical milling, nucleation and growth of the aluminide layer may be stalled.

The single-phase composition of the titanium aluminide layer is most likely a direct result of the thermochemical properties of the TiAl₃ phase formed. Of the three titanium aluminide phases for which thermodynamic data are available, TiAl₃ possesses the lowest free energy of formation. In a reaction where reactant material is unlimited, this predicts that TiAl₃ is the most likely to nucleate and form in abundance. This does not preclude the formation of other phases of higher free energy, however it does give some indication as to why TiAl₃ is so prevalent in the specimens.

5.2 SHS Reactions

The observations of the diffusion bonding work give some insight into the resulting morphology and chemistry of the aluminide layer produced in the SHS reacted specimens. Comparison of combustion temperatures relative to the melting point of the TiAl₃, suggests that the resultant microstructure of the aluminide layer is caused by a kinetic effect associated with the reaction rather than synthesis in the liquid state. Analysis of thermochemical data leads to an increased understanding of the mechanis=ms responsible for single phase growth in the aluminide layer, where exclusive nucleation and growth of TiAl₃ was attributed to the high negative free energy of formation of **t**the phase. Even conclusions regarding the resultant crystal structure of the product aluminide phase in diffusion bonding specimens is equally applicable to that formed in SHS reacted specimens. What remains to be discussed however, are the ignition temperature and exothermicity variations observed in time-temperature profiles yieldied from measurements taken for different heating rates.

From analysis of the thermal profiles presented in the previous section (Figure 4.19)_{\equiv} it appears that heating rate has a profound impact on the ignition temperature and exothermicity of the SHS reaction. This was made obvious from the increase in ignition temperature, and notable decrease in temperature rise associated with heating rates lowver than 25°C. Such a result suggests a significant change in reaction kinetics, more specifically, marking a possible change in reaction mode from SHS to combustion synthesis. This assumption is based on the analysis of initiation conditions required **t**for each type of reaction, and the evaluation of the procedure used to heat the specimens in this work.

As discussed in Chapter 2 (section 2.5), initiation of an SHS reaction requires the localized application of heat, at a point on the interface of the reactant species to elevate temperature to initiation of a reaction. Rapidly heating specimens in the Gleeble 1500 thermomechanical simulator has the potential to create such a scenario, by the generation of hot spots at surface asperities of the titanium and aluminum foils. Surface asperities, which are inconsistencies at the foil surface, serve as areas of high electrical resistance which restrict the flow of current through them. During resistance heating, this results in higher temperatures at these areas than in the surrounding material. As bulk temperature of the specimen is increased, so too is the amount of current which is forced to pass through it, further elevating the temperature at asperities above that of the specimen as a whole. This effect would become more pronounced at higher heating rates (presumably in excess of 20°C/minute), where the Gleeble is less capable of dealing with these small localized over-temperatures. On further heating, temperature of hot spots would reach the ignition point of the SHS reaction, subsequently initiating reactions that propagate across the specimen. The temperature measured at ignition would appear lower than the true ignition temperature for SHS reactions because measurements are taken at a point sufficiently far from the point of reaction initiation. This description fits the observed ignition temperature of samples heated at rates above 12.5°C/minute.

A requirement of the simultaneous combustion reaction, or thermal explosion, is the uniform distribution of temperature across the entire interface of the reacting species upon reaching the ignition temperature. Such uniformity of temperature is most easily achieved by slow heating of the reactant materials. The ensuing thermal explosion would then occur rapidly, dissipating heat quickly to the surrounding environment. At relatively low heating rates of 12.5°C/minute and 6/25°C/minute, sufficient time is provided to homogenize temperature throughout the specimen. Thus, in conjunction with smaller increments of temperature increase, hot spots observed in specimens heated at higher rates are less likely to occur. In the absence of any potential initiation sites for the SHS mode of combustion, heating continues to the point of simultaneous ignition of reaction at all reactant interfaces. Unlike those measured in samples heated at higher rates, the measured reaction initiation temperature more likely reflects the true value.

The observation of initial, or pre-cursory peaks is in agreement with the experimental work described in previous sections. It has been suggested that these reactions can be associated with the formation of titanium oxides. This becomes plausible when applied to the present work due to the low vacuum environment in which the SHS specimens were processed.

Table 5.1 summarizes the various heating rates utilized in the SHS experiments of this work, the ignition temperatures observed for specimens heated at these rates, and the presumed mode of reaction (SHS or simultaneous combustion) associated with reaction at the specific heating rate.

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Heating Rate (°C/minute)	Ignition Temperature (°C)	Mode of reaction
6.25	~589 (±5°C)	Simultaneous Combustion
12.5	~588 (±5°C)	Simultaneous Combustion
25	~549 (±5°C)	SHS
50	~566 (±5°C)	SHS
75	~570 (±5°C)	SHS
100	~563 (±5°C)	SHS

-

 Table 5.1: Summary of heating rate, reaction ignition temperature, and corresponding presumed mode of reaction.

Chapter 6

CONCLUSIONS

Based on the results and discussions presented in this work, the following conclusions have been drawn:

Diffusion Bonding

- The primary mechanism for aluminide formation in the diffusion-bonded specimens was combustion synthesis, brought about by saturation of titanium with diffusing aluminum atoms.
- Temperatures achieved by the combustion synthesis reaction were high, and approached the adiabatic temperature for the formation of TiAl₃.
- Grain boundaries, due to their high energies, are suggested to be primary initiation sites for the combustion synthesis reactions.
- Rate of aluminide layer growth demonstrated a strong parabolic dependence on time for a given annealing temperature. This defined growth as a diffusion controlled process.
- Morphology of the layer was initially globular, with degree of consolidation increasing with elevated annealing temperature and prolonged annealing times.
- Chemistry of the layer was confined exclusively to the TiAl₃ phase. This is suggested to be caused by the high negative free energy of formation for this phase.

 Cracking in specimens was likely caused by residual stresses induced by rapid cooling of specimens from the annealing temperature upon completion of processing.

SHS Reactions

- Exothermic reactions were initiated at the interface of titanium and aluminum foils.
- The magnitude of these reactions was found to decrease with decreasing heating rate. A significant increase in ignition temperature of the reaction was also observed with decreased heating rate. This was believed to be associated with a change in mode of the reaction from SHS to simultaneous combustion.
- Reaction resulted in the liquification and extrusion of un-reacted aluminum in most cases. This was caused by the high temperatures achieved by the reaction.
- SHS reacted specimens showed little variation in morphology over the range of heating rates tested. Aluminide layers consisted of non-consolidated bands of globules, ranging from 1 to 5 µm in diameter.
- Chemical analysis confirmed that the layers were composed completely of TiAl₃ phase. This single-phase chemistry was also attributed to the high negative free energy of formation of TiAl₃ relative to the other aluminide phases stable at the processing temperatures.

Suggested Future Work:

- 1. A detailed investigation into the binary diffusion of aluminum and titanium should be conducted. This would presumably entail marker experiments to qualitatively determine the predominant direction of diffusion.
- Techniques to more accurately measure the initiation and combustion temperatures of the combustion synthesis reactions should be developed, and experiments subsequently conducted.
- 3. Experiments designed to study the required annealing conditions for bonding of the converged aluminide layers should be conducted. This would complement the present work by detailing the final stages of composite formation.
- Mechanical testing, including 3-point bend tests, hardness, and fracture toughness testing should be performed on completed composite structures to gain insight into the mechanical behavior of the material.

Chapter 7

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