EFFECT OF MECHANICAL MILLING AND CURRENT INTENSITY ON
THE ELECTRICALLY ACTIVATED COMBUSTION SYNTHESIS OF
TITANIUM ALUMINIDES

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ABSTRACT OF THE THESIS

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Over a number of decades, titanium aluminide intermetallics have been of high scientific and industrial interest due to their good mechanical properties and oxidation resistance. Despite Ti3Al and TiAl receiving the vast majority of this interest, less work has been conducted on the Al3Ti intermetallics. In the present work, titanium aluminide (Al3Ti) has been reactively processed from elemental powder using a combined mechanical and electrical activation approach. The effect of mechanical activation and electric current intensity on the ignition and phase development is discussed. An increase in current intensity was found to result in an increase in product homogeneity and product porosity. A secondary reaction and sustained glow was found to occur only at the higher current intensity used, which in turn increased the product homogeneity. Ignition was not possible when powders were milled for short durations, while prolonged milling resulted in mechanical activation that promoted a self-propagating type ignition event. The time to reaction (where the whole compact was engulfed with the reaction wave) was found to decrease with an increase in current intensity. The compacts subjected to the highest current intensity of 1000A, possessed the lowest hardness due to the excessive porosity generated. Such materials maybe suitable for high-temperature oxidation resistant filter applications.
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CHAPTER 1

INTRODUCTION

The trialuminides alloys of several elements have been a point of interest as high temperature materials over a number of decades. This is only because these trialuminides can have low densities and their specific strength is also high [1]. Due to the high aluminium content present in these materials, they usually possess excellent oxidation resistance.

Even though these materials have high elastic moduli they still generally have very low ductility. The production of such materials by conventional methods is also very difficult thus powder processing techniques have been employed which are very expensive if a pre-alloyed powder is used. Hence combustion synthesis methods have been developed that make use of elemental powders and the exothermic heat generated due to their reaction. In these method the compounds are produced by initiating a reaction in the compact between the elemental powders for example aluminium and titanium elemental powders [2-4].

Factors such as composition, compacting methods and reaction initiating procedure have been studied and understood to have an effect on the rate of compound formation in combustion synthesis [5]. Another way of producing fine Al₃Ti compound powders directly from the oxide mixtures of TiO₂ and Al₂O₃ is by a calciothermic reaction using CaH₂. This procedure consists of three steps: raw oxide blending, co-reduction and leaching [6].

It is observed that, mainly Al₃Ti phase forms during combustion synthesis and TiAl and Ti₃Al phases form after homogenization. By addition of alloying elements to the aluminides, desired properties can be achieved as well as a variety of microstructures can be generated by heat treatment [7].

In recent years studies focusing on combustion synthesis processing of reactive powders shows that the heat of reaction can be utilized in the synthesis of aluminide intermetallics. Using these processes the temperature can be raised to very high temperature hence achieving fast reaction within a few seconds and uniform distribution of elements resulting in uniformity of stoichiometric composition of the alloy [8].
In addition to the above, research has been conducted on field and current activated combustion synthesis where the billet formed from elemental powder is heated through a field source or through direct current to form the desired intermetallic compound. The use of titanium and aluminium elemental powder has been proven useful than pre-alloyed intermetallic powder because firstly they are cheaper than pre-alloyed powders and secondly due to them able to generate exothermic heat from their reaction. The reaction energy is utilized for the synthesis of the intermetallic compound hence making it more energy efficient. Applying electric current with high current intensity to the sample increases the combustion temperature and due to this the formation of other phases is suppressed for a given starting stoichiometry [9]. The reaction taking place during this experimental condition often results in temperatures higher than the melting point of aluminium. Thus liquid aluminium is formed during the reaction and its reaction with solid titanium plays a crucial role in the synthesis of such intermetallic compound by powder metallurgy techniques such as combustion synthesis, reactive hot pressing, and also reactive hot isostatic pressing [4].

From the different intermetallic compounds observed in the binary Ti-Al phase diagram only Ti₃Al, TiAl and Al₃Ti are identified as materials which are good for application involving high temperature hence a notable amount of research has been carried out on these intermetallic compounds. Evident from the research among these compounds, Al₃Ti possessing low density, high microhardness (strength) and best oxidation resistance our research was conducted to produce Al₃Ti intermetallic compound from a premixed aluminium and titanium elemental powder with respective stoichiometry needed to produce our end product i.e. Al₃Ti [10]. The billets produced from the powder mixture with appropriate stoichiometry ratio are heated by application of direct electric current through the powder green compact and thereby achieving complete combustion. Here the intent is to heat the entire sample volumetrically to its ignition temperature with our electrical processing technique; thereby the whole sample is converted to the desired product.

By application of high current intensity to the sample, the green compact transforms to the product within a few seconds. Hence achieving fast reaction and high temperatures, which are usually greater than or around the melting point of aluminium. During the reaction the molten aluminium travels through the sample around all the titanium particles, where a reaction insures forming Al₃Ti. From all the researches involving reactions between Ti and
Al it is mentioned that from all the Ti-Al intermetallic compound Al₃Ti is the only intermetallic formed during the reaction where the process temperature ranges from 973-1273K [11]. However research reports that in some cases Al, Ti, and sometimes Ti₃Al, TiAl are also generated during the reaction.

In the present work we are investigating the effect of current intensity on the formation of Al₃Ti. We have also investigated the effect of green density on the conduction of electric current through the sample. As the reaction is an exothermic reaction and also due to the high current density, the temperature achieved is significantly higher under this condition, and the formation of different intermetallic compounds has been observed. The unique feature of the project, is the combined effect of mechanical and electrical activation on combustion synthesis of Al₃Ti. Here we use mechanically milled powder that provides for the mechanical activation. Characterization of the samples with different current conditions is examined in our work using namely Scanning electron microscopy (SEM), X-ray diffraction (XRD) and Energy dispersive spectroscopy (EDS). Finally hardness measurements were also taken for specimens produced under different current intensities.

This thesis report is divided into five chapters. Chapter 1 is an introduction of the research, Chapter 2 is a literature survey covering relevant background research conducted in the area, Chapter 3 states the novel aspects of the present work, Chapter 4 is experimental procedures and Chapter 5 is results and discussion. The thesis is finalized with a conclusion section and future scope.
CHAPTER 2

LITERATURE REVIEW

This chapter presents a brief overview of titanium aluminides, their compositions, their properties, applications and processing techniques. It also provides background on current and past research activities in the area of titanium-aluminium powder processing.

2.1 INTRODUCTION TO Ti-AL INTERMETALLIC COMPOUNDS

Among numerous trialuminides intermetallics, titanium aluminides are known to be lightweight materials that can compete in applications with super alloys and some ceramics. This is mainly due to their very low density, high melting temperature, very high specific strength, elastic moduli and other mechanical properties at high temperatures. In addition these materials also show excellent oxidation resistance in view of their high Al content. The crystal structure of all the trialuminides are low symmetry (tetragonal) DO_{22} or DO_{23} structures. By this low symmetry the available twinning systems and dislocation slips are restricted. For Al_{3}Ti the deformation takes place by twinning system [12].

The reaction between solid titanium and solid/liquid aluminium plays a vital role in miscellaneous technologies that are being developed to process and synthesize many advanced materials. Essentially the formation of Al_{3}Ti is facilitated by the exothermic heat generated during the reaction of liquid aluminium and solid titanium. Solid state reactions between solid titanium and solid aluminium can also occur during reactive sintering of elemental powder. This can occur if the heating rate is very low or the maximum temperature is below the aluminium melting point. In cases where there is formation of liquid aluminium in the reaction the trialuminide are produced even if the aluminium content is low in the green compact [13].

Figure 2.1 [11] of the binary Ti-Al phase diagram shows that there are several intermetallics compounds namely Ti_{3}Al, TiAl, TiAl_{2}, Al_{3}Ti, Ti_{5}Al_{11} etc. Among all these compounds Ti-rich compounds like Ti_{3}Al and TiAl are seen over a range of compositions. Among these intermetallic compounds formed in the phase diagram Ti_{3}Al, TiAl and Al_{3}Ti
are looked as futuristic materials for applications which require high temperature and low density [14].

The properties of different alloys of Ti-Al are shown in Table 2.1 [15]. From this we can conclude that since Al₃Ti has the lowest density, highest micro-hardness and hence strength. This compound has been selected as the model material for our research investigations.

### 2.2 MECHANICAL ALLOYING

Mechanical alloying is a technique used for the formation of homogenous powder material from blended elemental powder. It can also be considered as a solid-state powder processing technique. This powder processing technique involves ball milling of powder in a vial containing milling balls, the milling action is provided by a high-energy ball mill.
<table>
<thead>
<tr>
<th>Property</th>
<th>Ti$_3$Al alloy</th>
<th>TiAl alloy</th>
<th>Al$_3$Ti alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Critical ordering temperature (°C)</td>
<td>1100</td>
<td>1460</td>
<td>1350</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>1600</td>
<td>1460</td>
<td>1350</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>4.1- 4.7</td>
<td>3.7- 3.9</td>
<td>3.4</td>
</tr>
<tr>
<td>Young’s modulus (GPa)</td>
<td>120 – 145</td>
<td>160 – 176</td>
<td>192</td>
</tr>
<tr>
<td>Vickers Microhardness (Kg/mm$^2$)</td>
<td>180-350</td>
<td>180-450</td>
<td>465-670</td>
</tr>
<tr>
<td>Oxidation Resistance (°C)</td>
<td>650</td>
<td>800</td>
<td>1000</td>
</tr>
</tbody>
</table>


machine. Inside the vial, firstly the powder particles are deformed from the contact and impact between milling balls. Following deformation, the particles are work hardened and finally re-welded together again [16, 17]. To produce oxide dispersion strengthened (ODS) alloys this method was developed but it is nowadays used to generate alloyed powders of two or more different elemental powders as a start condition by atomic mixing. Variables for MA include ball- powder weight ratio (BPR), material and size of the ball, milling speed and milling atmosphere.

When reactive powders are ball milled, the powder reactants can experience an SHS type reaction which in turn changes the reactants to the desired product (s) inside the milling vial, This type of reaction is known as mechanically induced self-propagating reaction (MSR) [18]. If such powder mixture is milled for a period of time less than that which causes a reaction, then the powder mixture will still be in its elemental form and are referred to as mechanically activated powders. The processing of reactive powders can take many forms including mechanically activated self-propagating high temperature synthesis (MASHS) and mechanically activated annealing process (MA2P) [17]. These processes have been shown to produce largely porous compacts with refined microstructures. Mehra and Morsi have successfully ball milled Ti and Al powders in a way that no reaction has occurred between
them [19]. Morsi et al. [20] has also successful produced powder aggregates of Al and carbon nanotubes by varying the BPR and milling times in order to produce composite powders that were subsequently consolidated using a new technique called Spark Plasma Extrusion. By using the same technique Morsi et al and El-Desouky et al. [21] extruded aluminium where the aluminium powders had been previously milled for 3 min under argon atmosphere. The idea behind this short milling was to break the oxide layers around the aluminium powder particles which normally act as an insulating layer preventing the flow of electric current during electric current processing. Milling atmosphere has a major effect on the contamination of the powder. Thus powder can be milled in the vial under an inert gas such as argon or helium, which prevents oxidation. Nitrogen and hydrogen on the other hand are found to react with the milled powders, so it’s used has been avoided unless one intendeds to produce nitrides or hydrides.

Kyoung II Moon and Kyung Sub Lee synthesized nanocrystalline Al-Ti alloys using reactive ball milling in a hydrogen atmosphere. The powders used were -325 mesh aluminium and titanium, milling condition were 30 hours milling time and 250 rpm speed of milling attritor. The BPR was 65:1 and 2% steric acid was added as a process control agent. After the milling process they were able to produce aluminium and TiH2 with grain size less than 20nm. This powder was consolidated and hot extruded. Analyses shows that around 360-480ºC the TiH2 was decomposed and Al3Ti was formed during hot extrusion and the particle size ranged from 50-100nm. The high strength of reactive ball milled alloys was attributed to its very fine microstructure [22].

During MA the contamination of the powder increases by increasing the ball-powder weight ratio, speed of milling, milling energy and by use of a Process Control Agents (PCA). New surfaces are formed due to fracturing of powder particles following extensive plastic deformation. The particles subsequently also get cold welded together. In order to achieve good MA there by reducing the effect of cold welding, PCA is added to the milling powder mixture. These PCAs when added to the mixture get adsorbed on the surface of the powder particles inhibiting agglomeration between powder particles. They can be solid, liquid or even gaseous in nature [16].
2.3 Spark Plasma Sintering

Spark Plasma Sintering (SPS), is generally understood as a process of powder pressing (sometimes reactive pressing too), under application of electric current through powders which are subjected to constant or varying pressure at the same time. This process was developed in 1960s by Inoue et al. by an idea of using an electric discharge machine to sinter metals and ceramics [23].

A schematic of typical spark plasma sintering setup is shown in Figure 2.2 [24], the setup consists of a graphite die, in which powder is placed and both current and pressure is simultaneously applied through the use of graphite punches from either end. During the SPS process a pulsed DC current, DC or even alternating current is applied through the graphite punches. Such experimental setup is capable of applying pressure to the elemental powders in the die. Due to the electric current processing in SPS a Joule heating effect is developed which is responsible for the sintering of the powder. Also due to the current application in the SPS process the atomic diffusion rate increases significantly which leads to a high sintering rate i.e. making the sintering process faster [25]. SPS has numerous benefits to other conventional techniques namely rapid rate of Joule heating, generation of spark plasma, shorter sintering times, lower sintering temperatures, uniform heating condition and field effect on mass transportation [25-28].

The effect of electric field has been under significant investigation for decades due to the effects on crystal defect motion, growth, and crystal nucleation influenced by the electric field applied in the SPS process [29-31]. As SPS is limited to producing simple geometries due to its inherent geometric configuration its extension to spark plasma extrusion (SPE) has been proposed with an implication of producing extended geometries for powder-based materials [32]. Also under variable current conditions material re-crystallization can lead to grain refinement and the effect of stress induced deformation can produce geometries with new unique microstructures [33]. Hans Conard has also reported during the testing of very fine wire a decrease in the flow stress with an increase in current density [34].

2.4 Combustion Synthesis

A low energy direct synthesis process for the preparation of a variety of materials including carbides, intermetallics, ceramics and composites from compacts made of
elemental powder is termed as combustion synthesis (CS) which has very low processing temperatures and time [35]. This CS or Self-propagating high temperature synthesis (SHS) provides an alternative for the production of such advanced materials. The reaction occurring is an exothermic reaction which avoids the need for expensive equipment for processing also the heat of reaction is utilized in significantly raising the temperature of the reacting compact thus volatizing impurities with low boiling point, resulting in the formation of products with high purity. The maximum temperature achieved during the reaction is termed the “combustion temperature”. Combustion synthesis is normally divided into two modes of ignition. The first is termed self-propagating high temperature synthesis (SHS), where a powder compact is typically ignited at one end forcing a local exothermic reaction that gives off heat, which by itself heats the neighboring elemental powder layer to the ignition temperature, which in turn then releases heat which does the same as before. Hence the process is self-sustaining, where a reaction wave travels across the sample once ignited, converting reactants to products in an exothermic fashion, and hence the name SHS. Figure 2.3 [36] shows the schematic of SHS type of ignition. The other mode of ignition is when the
whole powder compact volume is heated uniformly to the ignition temperature. This is termed thermal explosion or volume combustion.

The earliest use of CS is dictated in 1825 by Berzelius using ceramic refractory material, he reports that by heating amorphous zirconium metal at low heating rates not red hot zirconium oxide can be manufactured below room temperature. In 1885, Goldschmidt obtained either metal or its alloys by reacting aluminium with oxides of chromium, titanium, zirconium and iron. He concluded that as aluminium oxide needs higher temperature than other oxides the aluminium metal will react with the metal oxides [37]. In the powder mixture of aluminium and phosphorous a piece of magnesium is inserted as an igniter to trigger the reaction, which in turn produces aluminium phosphide via SHS [38].

In 1964 [39] Krapf, introduced a process called chemical hot press. Here a mixture of reactive powder including an inert component and certain oxides are pressed in a die and using electric current and exothermic reaction is sustained through the powder mixture, the product was pressed by a uniaxial force and a dense material product was obtained. Another group of researchers, Stringer and Williams [40] synthesized a compound for a long duration in its plastic condition by combining the effect of pressing and exothermic reaction so that the product produced can be shaped quickly and easily. According to these authors the exothermic effect of the reaction in many cases is sufficient to form plastic product mass.
which can be deformed to the desired shapes quickly. The production of intermetallic compounds via SHS is also exemplified in the shape memory alloy NiTi compound, which has biomedical uses. Also these alloys were used as non-fusion aircraft couplings.

Ti-C and Ti-B composites were studied extensive during the early 1980’s, Logan studied the formation of materials such as TiC, TiB$_2$ and TiB$_2$-Al$_2$O$_3$ via reactive techniques [41]. One of the key leaders in SHS is Professor Z.A. Munir, with Holt he provided a fundamental understanding of combustion synthesis reaction [42]. His contribution to SHS includes: Combustion Synthesis of refractory carbides, borides, silicides, nitrides and intermetallic compounds (1980s). During 90s he determined kinetic parameters during SHS reaction by use of Boddington-Laye mathematical analysis. He also analyzed the role of thermal migration in pore formation during SHS reaction, analysis of origin of porosity in SHS products and the role of electric field in SHS reaction with experimental and modeling work. He theoretically analyzed the stability of self-propagating combustion synthesis waves by use of concept of SHS diagrams. His work using field activation includes synthesis of complex materials with simultaneous consolidation and micro-alloying. He also combined mechanical and field activation to synthesize dense nano-ceramics and nano-composites. He prepared nano-structured oxides for fuel cell application with SHS reaction using field activation. He also demonstrated that by combining spark plasma sintering and field assisted techniques nanostructure products with desired phase can be synthesized from nano-reactants and mechanically activated powders [43-56].

It is important to note that combustion synthesis is not only limited to titanium aluminides, in fact Ni$_3$Al and NiAl are another group of intermetallics that have been extensive researched. These materials also involve the melting of aluminium during their reactive processing. Various reactive methods in the past have been used for the production/consolidation of nickel aluminides using external pressure. Nishimura and Lui studied reactive sintering using compressive loads on Ni$_3$Al; the product included unreacted Ni, Ni$_3$Al and NiAl [57]. K. Morsi and S.O. Moussa investigated the microstructure and properties of Ni$_3$Al reactively formed under varying pressures and temperatures. In CS of Ni$_3$Al the compact prepared from elemental powder is heated near or above the melting point of Al i.e 660°C. Due to the reactive nature of the elemental powders an exothermic reaction then occurs. The transient liquid phase (eutectic/aluminium) melts and spreads converting the
reactants to products [58]. The author mixes nickel and aluminium elemental powder in the molar proportion of 3:1 in order to achieve desired Ni$_3$Al product. These powder mixtures were then isostatically pressed to produce green compacts with initial diameter of 13.2 mm and length of 23±1 mm with a green density of 76%. The reactive pressing experiments were conducted with the help of a compaction die and rams made of Inconel 718. The successful conversion of elemental powder compacts to Ni$_3$Al intermetallic compound in shown by Figure 2.4 [58].


The investigation window utilized to form these materials was from 1200ºC to 1000ºC after the reaction had occurred, and as the specimen was cooling from the combustion temperature. From the study, the importance of pressing time and temperature on product characteristic and properties was highlighted. With high temperature and pressure the total porosity decreases, hardness (HV) was increased and some grain growth was also seen [58].

The product obtained from SHS in the absence of externally applied pressure has poor density. K. Morsi and N. Wang came up with a novelty in the green compact design which provides a notable improvement in the density of synthesized Ni$_3$Al composite with 20% of TiC loaded on the sample with no external pressure [59]. Figure 2.5 [59] shows
improved microstructural design of green compact that allows efficient spreading of molten Al resulting in high product density without application of external pressure.

The authors suggested that by addition of ceramic reinforcement (titanium carbide: TiC) firstly, the presence of TiC will limit the motion of molten Al. Secondly, TiC particles provide cooling by acting as heat sinks thereby reducing the maximum combustion temperature. Both of these effect lead to the generation of more porosity and non-uniformity with an increase in TiC content. By the proposed new design for the green compact the authors synthesized products with porosity levels as low as 1.4% compared to 25% porosity product produced by combustion synthesis of conventionally mixed and pressed green compacts. The authors used a mixture of preferred stoichiometry in order to get an intended final product of Ni$_3$Al with 20 vol. % TiC after complete conversion. The conventional design uses the same powder mixture which is rotary mixed for 1.5 hours. While the authors use the same mixture but rotary mixes only Ni and TiC for 1.5 hours and ball mills mixture for 10 hours with tungsten cobalt balls in a Spex mixer under an argon atmosphere. These milled Ni-TiC composite powders are mixed in a rotary mixer for 1.5 hours with the Al to make up the balance. By ball milling the Ni-TiC powders mixture the TiC particles are trapped in between Ni Particles. Also it is reported that by increasing the milling time from 1 hour to 10 hour the powder shape changes from flaky external surface to smoother surface. This can be seen in Figure 2.6 [59].
With this new design the authors draw a number of conclusions. A near fully dense compact with porosity less than ~1.4 was produced. Vickers hardness of the product formed by the new green compact design is found to be over 5 times than the conventionally proposed product. Also with this new design Ni$_3$Al yield was higher than the conventionally prepared compact (Figure 2.7) [59].

2.4.1 Simple Combustion Synthesis

The reactant powders are mixed together and a powder compact is made, typically by pressing. These compacts are then ignited and the product is synthesized. The procedure includes 2 steps: for the first step the powders which are reactive in nature are mixed together with a specific stoichiometry ratio which affects the reactant produced later after the reaction. Different compounds, intermetallics, ceramics and composites can be manufactured via SHS reactions and are classified as follows [60]:

1. SHS elemental reaction systems: This method of reaction is the simplest and easiest of all the CS reaction which involves different elementals only [60].
2. Thermite-type reaction systems: One of the 2 type of thermite type reaction is the oldest and well known as “thermite reaction” which involves the reduction of oxides to elemental powder. Another type of thermite reactions involves the reduction of the element from the elemental oxide used which reacts with associated element forming a compound. Due to use of cheaper oxides reactants with expensive elemental reactants researchers have developed new interest in synthesis of advanced materials by this method [60].

3. Compound reaction system: In this reaction system at least one of the reactants used is a compound. A complex reaction has been reported when an oxide with higher valance i.e. higher is mixed to react with lower oxide of different metal [60].

2.4.2 Densification of Combustion Synthesized Materials

One of the lead disadvantages for synthesizing materials with SHS reaction is its inherent high porosity in the material components produced. It is useful for manufacturing powders, but it will be beneficial and economic if a dense or a net shape component can be produced with few steps using combustion synthesis. Due to high exothermic nature of the SHS reaction the atomic bonding the products is tighter compared to the reactants producing high density reaction products. These change in density of products and reactants give rises
to change in volume and increase in porosity. The process of solidification can also generate porosity i.e. if a material is in molten state during the reaction. Thus a higher exothermic reaction generates higher intrinsic porosity. Since SHS type reaction has high combustion temperature, we also see evaporation of metal taking place and due to some level of porosity already present in the green compact Extrinsic porosity is usually produced. By preheating the specimen before the combustion synthesis reaction a small amount of porosity can be reduced. Also by lowering the combustion temperature the possibility of producing liquid or gaseous phase in the SHS reaction is reduced hence reducing the porosity in the product. If a dense product is to be synthesized and the reaction has taken place in an inert environment it is necessary to remove argon from the pores in the product [61].

Since SHS reaction fails to produce products with high density, a number of techniques have been developed by applying pressure while the SHS reaction is taking place at high temperatures. This combined method of densification and combustion synthesis are used to manufacture hard-alloy components i.e. rollers, pressuring equipment, cutting inserts etc. These techniques are described below:

2.4.3 Pressureless Densification

In these processes a diluents is incorporated in the powder mixture which give no change or very less change in the volume if the reaction are conducted in vacuum. But with this method a fully dense material have not been produced yet. In CS type of reaction the temperature of the reaction can exceed the melting point of certain material [62].

2.4.4 Simultaneous Combustion Synthesis and Densification

During the SHS reaction the synthesized product can still be in a plastic state due to the high reaction temperatures (if above the ductile to brittle transition temperature). In order to densify the porous product, a suitable load is applied either after the reaction is completed or during the SHS reaction. The timing of load application has been found to have a major effect on the product quality, making it a crucial parameter in the process. If application of load happens to be early then gas produced during the reaction cannot escape from the specimen giving rise to highly porous product. Also since the product synthesized by SHS
reaction cools down rapidly, if the load is applied too late it becomes harder to completely consolidate the product.

2.4.5 Combustion Synthesis and Vapor Transport

The one simple way to produce a vapor transport medium is by conducting SHS reaction within a reactive gas environment. Another way to produce a medium is selecting the reactants or the products which are unstable at the high temperatures generated during the SHS reaction. With this method the reactants condense and form new morphologies such as sub-micron particles and whiskers. It also adds some considerable kinetic advantage to the reaction [63].

2.4.6 Thin Films and Coatings

SHS reaction is applied on substrate materials to produce thin films and coatings. These coatings can serve towards the improvements of some chemical, mechanical or physical properties related to the surface. Such thin film can be can be produced by depositing reactant layer using PVD sputtering, it can also be produced spreading the layer of the powder mixture used and then pressing it on the substrate or by placing thin foils of the reactant and pressing onto the substrate [60].

2.5 Effect of Process Parameters in Combustion Synthesis

Various types of reaction parameters affect SHS type of reactions, i.e. powder particle size, stoichiometry ratio, density of green compact, thermal conductivity, ignition temperature, combustion temperature, cooling rates and state of reactants. Some of these parameters are interdependent.

2.5.1 Powder Size and Powder Shape

Normally the SHS type of reactions is carried on samples which are made from powder. Thus particle size and shape play very crucial role in maintaining the porosity level, size of the pore, thermal conductivity of reactants and products. When two different particles sizes of powders are used one small and the other big then the powders with small particle size are packed in-between the larger ones which ultimately give rise to high packing density, also by this method the porosity and pore size is reduced too. With the decrease in particle
size the surface area is increased which increases resistance to compaction. Due to short range weak forces between these small particles the inter-particle cohesion increases thus increasing agglomeration. If high loads are applied during the packing/compaction process the density and the strength of the green specimen is also increased. This is because when an external pressure is applied the particles deform into a high density form. In liquid phase sintering the interactions of packed particles are of concern. In between the solid particle and a liquid state of particle the forces between the two solid particles which has liquid present in between it leans on the contact angle between solid and liquid which is termed as “wettability”. As indicated in Figure 2.8 [64] when the forces between the two solid particles are repulsive in nature and the liquid present in between them is in convex shape then the contact angle \( \alpha \) is high. If the forces between the two solid particles are attractive in nature and the liquid between the two particles is of concave shape than the contact angle \( \alpha \) is smaller. This force is also dependent on surface energy of the liquid present in between the particle and the volume of the liquid [64].

![Figure 2.8. Dependence of inter-particle force on wettability: (a) repulsive non-wetting force; (b) attractive wetting force; \( \alpha \) is the contact angle. Source: Moore, J. J., and H. J. Feng. “Combustion Synthesis of Advanced Materials: Part I. Reaction Parameters.” Progress in Materials Science 39, no. 4 (1995): 243-273.](image)

The distance between the two particles and the volume of the liquid also affects the capillary force. The capillary force pulls the particles trying to achieve denser packing and the liquid provides lubrication for particle rearrangement. If the particle sizes are small the capillary force is high for the system and it has less amount of liquid between the particles with a less contact angle. The force increases when the particles are approaching each other.
and the energy is lowest when the wet particles are in contact with each other [64]. This is shown in Figure 2.9 [64].

![Figure 2.9. The effect of (a) liquid volume between two particles and (b) particle separation on the inter-particle capillary forces, \( r \) is the radius of the particle, \( \delta \) is the distance between two particles and \( \gamma \) is the surface energy. Source: Moore, J. J., and H. J. Feng. “Combustion Synthesis of Advanced Materials: Part I. Reaction Parameters.” Progress in Materials Science 39, no. 4 (1995): 243-273.](image)

2.5.2 Processing of Reactant Particles

The green compacts prepared form powders are affected by shape and size of the powder particles used and also from the powder handling method and compaction techniques. The morphologies and properties of the product depend on the compaction of green powders. In order to ensure that the product structure is uniform the complete mixing of reactant powder is necessary. The products formed from the SHS reaction can contain microstructural imperfection i.e. micro-porosity, lamination and cracking. The main causes for product porosity are:

1. The gases or the impure volatile reactant produced during the CS reaction can lead to some of the imperfections.
2. During the CS reaction the volume of the product changes from the green compact and can lead to generation of intrinsic porosity.
3. The presence of some green porosity can be carried over to the product
4. Micro pores are also produced due to vacancy diffusion.

Also poor homogeneity of the green compact microstructure can lead to inhomogeneous product microstructures; this is mainly due to poor powder mixing. It is
therefore important to point out the importance of powder mixing and green compact production prior to reactive processing. Dry powder processing techniques are typically used, where agglomeration is noticed in the powders which are of varying size. Such agglomeration is caused by Van der Waals a attractive force which is observed between the powder particles. These can give rise to poor mixing of the reactant mixture leading to the production of non-uniform microstructures of products. Depending on the characteristic of the required product powder structure powder can be mixed via vibration, rotation, ball milling or even V-blended machines. The powder mixture is then pressed in a die, to produce the green compact. But in a few cases (especially for very fine powder) it is extremely tough to achieve high uniformity in the green compact microstructure hence a wet powder processing approach is utilized to enable thorough mixing. In this process the powders used are dispersed in a liquid in a way that the powder particles are free to move in liquid depending on how viscous the liquid is and what amount of powder particles are added in the liquid. After the powders are added in the liquid a powder suspension is produced generally by ultrasonic mixing using high frequency. These powders which are mixed avoid the formation of agglomerates, as the agglomerates are easily broken up. This suspension is finally slip cast or pressure cast in a porous mold and allowed to dry producing a green body after removal from mold [64]. Another way is to mechanically disperse the ultrafine powder using mechanical milling, as mentioned earlier.

The density of the green compact produced through these different techniques can vary from each other, thus a compact prepared from different technique will have different thermal conductivity, which can affect SHS processing. Green compacts prepared by using ultrasonic vibration methods is reported to have increased green density and decrease in the time of the reaction if powder with bigger particle size is used. Research has shown that the green density affects ignition and rate of reaction propagation. It is reported that the propagation rates and combustion temperatures decrease as the green density increases. The change in the density of green compact affects the microstructure of the final products.

During a conventional combustion synthesis reaction of 3Al+Ti to produce Al$_3$Ti intermetallic, it had been observed that Al melts first, this Al travels through the pores of the green compact using the capillary forces. But if the density of the green compact is too low then the capillary forces are reported to be weak and as the particles are apart from each other
due to low density can also give rise to incomplete reaction. In this case Ti would be surrounded by the layer of thick TiAl phase and another layer in between them of Al$_3$Ti which looks like an annular ring is formed. But in case of high green density the molten Al spreads through the sample quickly and completely between Ti particles giving rise to whole Al$_3$Ti grain [65].

At high combustion temperature during SHS reaction if impurities or moisture is found on the surface of the particles the evolution of gases from the sample may lead to structural imperfection in the product i.e. gas channels, cracks, voids or even complete destruction of specimen. To avoid such imperfections in the final SHS product the compact undergoes a pre-combustion treatment. This pre-combustion process involves heating the green compact (with a high level of interconnected open porosity) or the reactant powders in vacuum to a certain temperature to evaporate adsorbed humidity on the powder surfaces for a few minutes or for several hours [64].

The stoichiometric ratio used for the reactant powder mixture is also one of the important process variables affecting the SHS reaction and its products. A slight deviation in the stoichiometry ratio required to synthesize the desired product would result in a decrease in the combustion temperature i.e. any overdose of either of the reactant powder can decrease the rate of exothermic reaction. The use of an excess or deficiency in reactants as mentioned earlier reduced the rate of exothermic reaction thereby reducing the combustion temperature and sometime produces unpredictable products [65].

### 2.5.3 SHS Ignition Techniques

To initiate an SHS type of reaction there are plenty of techniques, for example initiating the reaction by use of chemical oven, laser radiation, radiation from heating coil, radiant flux spark etc. Radiant flux type of ignition provides a standardized condition for each ignition reaction. A typical ignition technique consists of radiation/ignition source, a shutter to control the radiation and a window of quartz or any other material. If large heat flux densities are needed then laser-induced ignition is used. In chemical ignition the combustion process is initiated when the heated sample is brought in contact with reactive gases or liquid reagents with a sufficient heat. In order to select the most efficient or
appropriate ignition system the main criteria to select the system should be what system needs to be investigated [65].

2.5.4 Heating Rate

The combustion synthesis reaction is influenced by the heating rate which is completely dependent on the input power. A decline in heating power causes an increase in the time required to heat the sample before the ignition is initiated increase. Also the rate of the reaction front increases with the increase in ignition power. When the ignition power used is high, the temperature at the interface between the compact and heat source increases immediately compared to the rest of the compact. Because of this when the ignition starts propagating most of the energy is lost to heat the cold unreacted sample which in turn leads to a non-uniform and non-equilibrium microstructure for the final SHS product which is identical to that produced at low green density compact. Similarly the microstructures seen from the product of a high green density compact are achievable by using low ignition temperature so that the entire sample gets pre heated first leading to fully reacted and homogenous microstructure [65].

During the study of Ti-Al reaction system with different stoichiometry Moore et al. found that there are two steep peaks in the temperature profile of the reaction indication 2 exothermic reactions. In his investigation Moore et al. studies 4 different composition of Ti-Al with different stoichiometry ratio which were homogeneously mixed and then pressed into pellets of 8 mm diameter with a green density of 70 ± 2%. The samples were heated in an argon environment with a steady heating rate until the reaction is initiated between the elemental powders. When the Al-Ti compact was heated at a rate of 10 K min-1, the first exothermic peak was seen at 550 ºC with a combustion temperature of the reaction around 630 ºC. And the second exothermic peak was seen at the melting point of aluminium with a much higher combustion temperature as shown in Figure 2.10 [66].

When the heating rate was 15 K min-1, the first peak was found to occur at 520-570 ºC which is just under the melting point of aluminium (660oC). It was also found that the first peak occurred when the heating rate were as low as 2 K min-1. For the second peak the ignition temperature is close to the melting point of Al and the heating rate is 10 K min-1 or less. Also in some cases with high heating rates such as 50 K min-1 the second peak starts
below the aluminium melting point. In case of TiAl reaction with the chance in heating rates both ignition temperature and combustion temperature shows little change. But for Al₃Ti reactions, the product was solely Al₃Ti phase at all heating rate as seen in Figure 2.11 [66], also the product density of Al₃Ti changes more dramatically i.e. as the heating rate increases from 2-50 K min⁻¹ the density increase from 29 to 58 %.

They also report no significant changes in the ignition or combustion temperatures of with variation in TiAl composition. But the product densities decreased with an increase in aluminium content even at the same initial green densities. Figure 2.12 [66] shows the plot of relative density versus aluminium content (heating rate of 10 K min⁻¹). Also Ti₃Al and TiAl + Ti₃Al specimens maintains their cylindrical shape after the reaction, but in case of Al₃Ti and TiAl + Al₃Ti specimens are found to be bloated after the reaction. This clearly indicates that the bloating is occurred by the aluminium content not by the titanium content.
Figure 2.11. XRD patterns of the TiAl3 product under different heating rates (a) 2 K min⁻¹ and (b) 50 K min⁻¹. (□) Al3Ti. Source: Yi, H. C., A. Petric, and J. J. Moore. “Effect of Heating Rate on the Combustion Synthesis of Ti-Al Intermetallic Compounds.” *Journal of Materials Science* 27, no. 24 (1992): 6797-6806.

The results from the investigation suggest that there is no formation of any compound at the first peak and the formation of Al₃Ti compound is above the aluminium melting point. Moore proposed that the first peak is due to decomposition of hydrated aluminium oxide. The elemental powder physically adsorbs hydrated aluminium oxide which is shown as follows:

\[
\begin{align*}
\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O} &= \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} \\
\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O} &= \text{Al}_2\text{O}_3 + \text{H}_2\text{O} \\
3\text{H}_2\text{O} + 2\text{Al} &= \text{Al}_2\text{O}_3 + 3\text{H}_2 \\
\text{H}_2\text{O} + \text{Ti} &= \text{TiO (TiO}_2) + \text{H}_2
\end{align*}
\]
The formation of water vapor and hydrogen gas is responsible for the first peak if the green compact is heated first before the reaction than there is no first peak. Also the lower density for the high aluminium content is due to the more production of these gas and vapor during the reaction [66].

With the increase in heating rates initially we see the decrease in ignition temperature and increase in combustion temperature. But Gasparyan and Shteinberg [67] have observed during a similar SHS reaction conditions that at slow heat rates there are two different peak separated at 640 °C in the time-temperature plot. Heating rate not only influences the SHS reaction mechanism, but its reaction conditions and some intermediate reactions that take place also influences the SHS reaction mechanism. Knyazik et al. [68] developed a new method termed electrothermal explosion, in this method the powder mixture considering reactive powder mixture is heated by application of electric current through the specimen, in order to study the effect of heating rate on Combustion Synthesis of TiC. The research
reports that TiC synthesized are generally formed when there is a reaction of liquid Ti with the carbon to form carbides usually below the melting temperature of Ti.

### 2.5.5 Effect of Pressure and Temperature

Gupta et al. [69] investigated “the effect of pressure and temperature on phase transformation and properties of titanium aluminide obtained through reaction synthesis (RS)”. In their investigation pressure-assisted combustion synthesis was used to develop gamma titanium aluminide (Ti-48 at.% Al) using elemental powders. The condition for low temperature and pressure is 923 K and 7 MPa - 21 MPa while the condition for high temperature and pressure is 1023 K and 55.5 MPa - 111 MPa on a 30 mm diameter cold pressed sample at 60% green density before the RS experiment. The XRD results for the low pressure and temperature (LPT) shows the presence of residual Al and Ti along with rich Al3Ti phase, small peaks corresponding to TiAl is also noticed. Unlike the presence of remnant Al in LPT there is no Al for high temperature and pressure (HPT). Also for HPT the reaction proceeds beyond Al3Ti and forms TiAl and Ti2Al phase [69].

As the reaction reaches the melting point of aluminium, a transient liquid Al is formed which give rise to exothermic chemical reaction between Ti and Al forming Al3Ti. This exothermic reaction causes a temperature rise and accelerates the reaction to form series of aluminides. The imbalanced diffusion of Al and Ti leads to Kirkendall porosity thus the experiments conducted with almost no pressure show swelling. The homogeneity of samples is found to be improved as the applied pressure increases. Both LPT and HPT condition exhibits less oxidation resistance than the homogenized samples. While the HPT samples exhibits better oxidation resistance than LPT. This detrition in the oxidation resistance is due to the porosity, non- homogeneity and presence of elemental phase with sample of LPT [69].
CHAPTER 3

SCIENTIFIC/ENGINEERING NOVELTY

ASPECTS OF THE RESEARCH

This research involves the following novelty aspects:

1. This is the first study to examine the effect of electric current intensity on the CS of Al$_3$Ti intermetallic.

2. This is the first study to combine mechanical activation with electric current activation in the synthesis of Al$_3$Ti compounds.

3. A processing – microstructure property relation is presented for the electric current activated CS of mechanically activated 3Al+ Ti compacts.

4. First study to attempt encapsulation of titanium with aluminium during ball milling.

5. The first study to report a second glow occurred during the reaction electric-mechanical processing at 1000 A current.
CHAPTER 4

EXPERIMENTAL PROCEDURE AND
EQUIPMENT’S USED

4.1 POWDERS USED

Aluminium and Titanium powders were used for processing Al₃Ti intermetallics. The titanium powders used for this research were bought from Atlantic Equipment Engineers, USA. Aluminium powder used was bought from Alfa Aesar, USA. The specifications of both the powders were -325 mesh with average particle size of 7-15 micron with 99.9% purity.

4.2 WEIGHING OF POWDERS

The commercially available powders were weighed using a scale with accuracy of 0.0001g on plastic pan. The total weight of the mixed powder used was 20 g. After weighing the powders are homogenously mixed. The scale is shown in Figure 4.1.

4.3 DEGASSING AND MIXING OF POWDERS

After the appropriate mixture of aluminium and titanium is weighed this powders are kept in a vacuum degassing chamber shown in Figure 4.2. The chamber is equipped with a heating source which heats the chamber up to 220 F. This chamber is connected to the vacuum pump which sucks the evaporated gases such as moisture, oxygen etc. and releases it outside the chamber making it a vacuum degassing chamber.

For our first set of experiments the degassed powders were mixed in a Rotatory mixer at 70 rpm for 30 min. The rotatory mixer is shown in Figure 4.3, in order to mix the powders they are first stored in a plastic or glass container with a lid and then the container is kept in the big aluminium cylinder with cushion around it. This equipment facilitates dry and homogenous mixing.

4.4 BALL MILLING OF POWDERS

For the rest of the set of experiments ball milling of the powders was carried out. For this purpose a stainless steel vial have been used which is filled with a batch of 20gm of
Al₃Ti weighed powders (mixed according to the stoichiometry ratio). Stainless steel milling balls were used for MA process. The weight of the ball is 1.06 g and the diameter of the ball is ~6.35 mm. As the elemental powders are reactive powders a Process Control Agent (PCA) was added during the MA process, 0.3 g of methanol was added to the 20gm of powder mixture in order to avoid agglomeration and avoid reactive ball milling. At first the 0.3 g of methanol is poured in the vial and the vial along with weighed powders are kept in the glove box. The glove box is used to create an oxygen free environment, so the glove box is filled with argon gas ensuring that the MA process is carried out in argon atmosphere avoiding oxidation of the powders. After the glove box is filled with argon the mixed powders are then poured in the vial along with the milling balls. The Ball to Powder ratio used was 1:5.3. This vial is covered with a lid with O-ring around, it ensure the gas does not escape while Mechanical milling, and placed in a SPEX 8000 mixer/mill for the ball milling. Figure 4.4 shows Hardened steel vial with the Stainless steel milling balls, Figure 4.5 shows the SPEX mixer.
For the second set of experiment the 20gm of Al3Ti mixture is milled for 3 mins. For the third and fourth set of experiment the milling time is 60 minutes with a 15 min milling time and 15 min cooling time. For the same, the amount of aluminium added initially is 66.66% and 75% respectively with the total titanium. After 45 minutes of milling the rest of the aluminium is added 33.33% and 25 % for third and fourth set respectively. All the procedure of adding powders is done in glove box under argon atmosphere. Also the amount of PCA (0.3 g) remains the same. The main reason to change the composition of aluminium is to see which one gives better encapsulation of titanium surrounded by aluminium. Same milling balls and milling vial were used to prepare powder mixture for these sets of experiments. As the amount of aluminium changes for 45 mins of milling time the Ball to Powder ratio also changes. For the thirst set of experiments the initial BPR is 1:6.7 and for
Figure 4.3. Rotatory mixer at AMPL, SDSU.

Figure 4.4. Stainless steel milling ball & hardened steel vial.
fourth set of experiments the Initial BPR is 1:6.28. The final BPR ratio remains the same 1:5.23.

4.5 Compaction of Powders

The compaction die as shown Figure 4.6 produced a compact of 19 mm in diameter. The carver press at Advanced Material Processing Laboratory, SDSU shown in Figure 4.7 was used to apply pressure to the die which produces the green compact. The two rods on the left the shorter punch is the bottom piece which is steady and the long one is the pressure ram which is placed after the powder is poured to apply pressure from the press. Before compaction the surface of the cylindrical punches and the inner surface of the die is thoroughly washed with acetone and coated with lubricant.

The lubricant used is like a thin paste and made from mixture of acetone and Zinc Stearate. This lubricant when after being applied is allowed to dry for couple of minutes. Once dried the shorter punch is placed at the bottom of the die. An approximate of 9.8gm of milled/mixed powder according to the experimental condition is poured in the die carefully from the top side. During and after pouring the die is required to be tapped from the sides so
Figure 4.6. Compaction die used to produce 19 mm green compact.

that gas and space in between the particles can be voided. Once the powder is poured the longer punch is than placed form the top side. This die now is placed on the platform of the Carver press as shown in Figure 4.7 and a desired pressure is applied. Once the pressure is reached wait for a few seconds to release the pressure this is done to stabilize the pressure inside the die. The compacting pressure used to produce a compact of ~19 mm diameter, ~1.4 mm of height and ~74% ± 1% of green density is 170 MPa.

4.6 EXPERIMENTAL PROCEDURE

After the green compact is pressed, using a drilling machine a hole is drilled in the center of the cylindrical surface of the compact. The brill bit size used is 1.17 mm. This hole is drilled so that the temperature of the compact can be measured at a giving condition during the reaction i.e. In situ temperature measurements.

In order to measure the temperature of the compact the tip of a K type thermocouple is inserted in the hole and the other end of the thermocouple is attached to analog side of the Data Acquisition System. For our experiments Omega model no OMB-DAQ-55 was used as a data acquisition system as shown in Figure 4.8.
Figure 4.7. Carver press at AMPL, SDSU.
The power source used in the research is shown in Figure 4.9; this is a DC power source regulator which controls the input current for the experiment. The power source has a separate adjustment knobs for voltage and current the maximum voltage and current condition that can be achieved by this power source is 10 V and 1000 Amps. For our experiment procedure the voltage is set to maximum and the current conditions are varied as 600 A, 800 A and 1000 A. The current knob in the power source is set at 600 A in such a way that as soon as the power is turned on for the power source it would pomp 600 A current within a matter of second, it can also vary due to change in resistivity of the sample.

Tungsten Carbide-Cobalt is used as an electrode in our research. Figure 4.10 shows the schematic of the experimental setup. The green compact is placed in between the tungsten carbide-cobalt rods. Thermocouple placed in the sample gives the temperature reading during the experiment via Data acquisition system. The whole schematic shown is placed in the Instron which provides a constant pressure of 0.1 MPa from the top; it is shown in Figure 4.11. A thick mica sheet is placed between the Instron and the metal blocks at top and bottom surface of the Instron so that the applied current does not pass through the Instron and damage the machine. The power source is connected to the metal blocks. The whole schematic shown in Figure 4.10 is enclosed in an acrylic chamber designed in such a way
Figure 4.9. Power source at AMPL, SDSU.

Figure 4.10. Schematic of the experimental Setup.
that it covers from the top when the constant load is applied to it this can be seen in Figure 4.11.

The aim to put the schematic in the enclosed acrylic chamber is to conduct the whole experiment in an argon environment so that we can prevent oxidation during the reaction. Since the acrylic chamber designed could not completely seal the argon, hence a constant flow of argon is maintained during the complete reaction and also the chamber is allowed to be filled with argon before the reaction is triggered so that there no possibility of oxygen in the chamber.

### 4.7 Post Analysis Processes

After conducting experiments on green compact at different current conditions the product is prepared for analysis. First the specimen is sectioned from the center length wise using a diamond saw. Figure 4.12 shows Buehler Isomet 1000 diamond saw cutter used to section the specimen. Lower rpm were used to cut the specimen i.e. 600 rpm. The tip of the blade is needed to be kept wet during the cutting process, so 9 parts of water is mixed with 1 part of cutting fluid and filled in the saw, hence giving a smooth cut in the specimen.
This sectioned specimen is cleaned in ultrasonic cleaner and then heated in an oven to get rid of the water absorbed. The time to heat the specimen was 5 – 10 minutes just to make sure there is no moisture absorbed by the specimen. This dry specimen is then placed in the mounting presses.

The mounting press used is shown in Figure 4.13, it is a Leco PR-32 mounting press. The mounting material used is Bakelite. The time required to make the mount is 10 min.

Figure 4.14 shows the sample after mounting sequence the indent seen in the image is the indent made for hardness measurement. The reason to mount the specimen is that we can have a firm grip will preparing it for material characterization. The first step for preparing sample for Microscopic characterization is to grind the specimen finely. Since we make a cut on the specimen before 1-2mm ahead of the area of the interest, grinding helps in removing the excess material. Moreover, it helps to remove the damaged portion claimed by cutting operation and to make a flat and even surface which is essential for the microscopic characterization. Silicon carbide grinding papers were used for grinding the specimen. We started with 240 grit grinding paper, then 400 grit, 800 grit and finally the finest grit was used 1200 grit which is equivalent to ~7-8 microns. The time taken on each grinding was not fixed; it was done till we get assured that we have an even surface.
Figure 4.13. Leco mounting press at AMPL, SDSU.

Figure 4.14. Specimen after mounting in Bakelite.
After the grinding of the specimen polishing is carried out. The instrument used for both grinding and polishing is shown in Figure 4.15. Leco spectrum system 1000 is an automatic polisher and grinder. The polishing cloth and grinding paper used have a sticky back, this way it sticks the rotating disk and we can use the instrument for both grinding and polishing. Since the grinding involved is done till 7-8 micron, we start the polishing from 6 micron diamond suspension followed by 1 micron diamond suspension. The specimens which are polished have very smooth surface and no cracks. Also the polishing cloth was changed after the use of 6 micron suspension in order to avoid cross-polishing. The time set for polishing was decided on the basis of fine surface and mirror polish achieved. The suspension liquids are applied at a regular interval to enhance surface finish and to maintain constant material removal rate. After every stage of grinding and polishing the specimen is cleaned using ultrasonic cleaner shown if Figure 4.16 to avoid contamination of cloth and achieve food surface finish.

![Grinding and polishing machine at AMPL, SDSU.](image)

### 4.8 PRODUCT ANALYSIS/CHARACTERIZATION

Characterization and analysis of the product using different technique and equipment is conducted. They are as follows:
4.8.1 Scanning Electron Microscopy

Scanning electron microscopy of the polished specimens was conducted to see the intermetallic phase formed by the reaction and to see the change in porosity of the specimen. The Scanning Electron Microscope (SEM) images were taken with the help of FEI Quanta 450 FEG Scanning Electron Microscope, shown in Figure 4.17, in the Electron Microscope facility at San Diego State University’s Biology Department. The training for the use and operation of microscope was held by Dr. Steve Barlow.

Energy Dispersive Spectroscopy (EDS) analysis of the specimen is also done using the same SEM. EDS is a techniques applied to analyze the elemental composition of the entire specimen or an area of specific interest on the specimen. This analysis is considered to be the most compelling tool for microanalysis of elemental composition. The attachment used for the EDS is an Oxford INCA Energy Dispersive Spectrometer with 50mm SDD crystal.

4.8.2 Porosity/Image Analysis

For porosity and image analysis the backscattered images obtained from the SEM were used. For the image analysis UTHSCSA Image tool version 3.0 was used. To get the porosity calculation these steps were followed. At first the backscattered image obtained from the SEM is colored to gray scale. After that the threshold is adjusted manually to convert perceived pores into red pixels after adjustment of the threshold the red pixels are
converted to black pixels and the remaining pixels are white. The plugin in the software calculates the percentage of black pixels within the image.

### 4.8.3 X-Ray Diffraction of Powders

The machine used for XRD analysis is Philips X’Pert Pro shown in Figure 4.18 at Geology Department, SDSU. The X’Pert Data collector software is used to identify the peaks of composition the unidentified peaks are identified manually using the d-spacing of the corresponding element. The plot obtained from the XRD is against sin-theta to peaks count. The small chunk of the specimen is scrapped out of the specimen and is broken in to small powder as possible with the help of acetone and a grinder. The powder specimen with the acetone is spread on the glass slide and the glass slide is mounted inside the XRD machine for analysis. The mounting for the slide setup is shown in Figure 4.19
4.8.4 Hardness Measurement

The hardness measurement is carried out for the polished samples. For this purpose the Wilson Instrument Rockwell 574 shown in Figure 4.20 has been used. To measure the hardness indents are made using a 1/16” ball intender in the center of the specimen. The dwell time was 2 seconds. The minor and major loads are 10 kgf and 60 kgf respectively. The hardness measured is the average hardness of all the measured hardness on each
Figure 4.19. Mounting the specimen slide on XRD machine.

specimen. The space between the two indents on the surface was at least 3 times the size of the indent.
Figure 4.20. Rockwell 574 Wilson Instrument at AMPL, SDSU.
CHAPTER 5

RESULTS AND DISCUSSION

5.1 POWDER PREPARATION AND CHARACTERIZATION

The titanium and aluminium powders are the pre-cursor material used in the research. Figure 5.1(a and b) shows the scanning electron micrographs with their relative sizes and morphologies of the powder. For titanium the shape of the powders used is angular from Figure 5.1 (b) while for aluminium the shape of the powders used is ligamental from Figure 5.1 (a).

For the first set of experiments these aluminium and titanium powders are mixed in a rotatory mixer at 70 rpm for 30 in the composition of Al$_3$Ti. No degassing is done on the powders used. The compact made from this powder is than subjected to the experimental procedure at 1000 A current conditions. But the experiments conducted were not successful because there was no conductivity in the sample. The reason concluded for this is due to the oxides layer around the powder particles is producing more resistance.
To avoid this conductivity issue, a second set of experiments were conducted in which the powders were not mixed in the rotatory mixer any more. Instead these powders were milled in the SPEX milling machine. The powders were milled in the steel vial for 3 minutes so that the oxide layers can be broken giving us conductivity in the specimen. The milling time could have been more than 3 minutes but to avoid the risk of agglomeration the milling time is decided for 3 minutes. Figure 5.2 shows the micrograph of the green compacts milled for 3 minutes.

![Figure 5.2. Scanning Electron Micrograph for 3 minutes milled green compact.](image)

Experiments were conducted with the green compacts at 1000 A current condition. The specimens turned to red hot in color. The temperature measured with the help of K-type thermocouple is indicated above 1200 °C, but the sample did not react. Figure 5.3 shows the SEM image of 3 minutes milled un-reacted specimen, however on further investigation of the electrically processed 3 minutes milled specimen by SEM and EDS shows small amount of
Al\textsubscript{3}Ti was found in some parts of the microstructure. Figure 5.3 (a) shows the images at low magnification i.e. 200X and (b) shows the Al\textsubscript{3}Ti at high magnification i.e. 1000X.

Since the total volume percentage of the Al\textsubscript{3}Ti seems to be less the XRD scans were not able to detect it. Also the resolution limit of XRD is limited to ~3 volume percentage. This can be seen in Figure 5.4.

From the Figure 5.4 it is clear that the XRD was not able to pick up peaks for Al\textsubscript{3}Ti. Moreover there is no formation of any other face in the unreacted specimen. By comparing the XRD scans of both green compact and unreacted compact it can also be concluded that there was also no formation of other intermetallic phases after 3 minutes of milling. Now from the experimental results of 3 minutes milled these set of experiment were also unsuccessful.

Since both milled and unmilled powder compacts were unable to react. We came up with a novel aspect to encapsulate the titanium particle with aluminium around it. So other two sets of experiments were conducted in these. For these set of experiments first the powders are degased in the vacuum degassing equipment at AMPL for 3 hour at 225 F. After powder degassing to observe the rate of incapsulation, the addition of aluminium in whole amount of titanium (7.44 g) was done with two different amounts. Table 5.1 will simplify the process.
Figure 5.4. XRD Scans for 3 minutes milled green compact and un-reacted specimen.

Table 5.1. List of Powder Preparation Techniques for some Samples

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Vacuum Degassing</th>
<th>Initial amount of Al For total of 20gm Al₃Ti</th>
<th>Final Amount of Al for total of 20gm Al₃Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA 2/3</td>
<td>3 hr</td>
<td>8.38</td>
<td>4.18</td>
</tr>
<tr>
<td>MA 3/4</td>
<td>3 hr</td>
<td>9.42</td>
<td>3.14</td>
</tr>
<tr>
<td>MA 3/4:1/4</td>
<td>No degassing</td>
<td>12.564</td>
<td>0gm</td>
</tr>
</tbody>
</table>

Both the samples MA 2/3 and MA 3/4 were successfully reacted via electrical processing with same current condition, it was difficult to choose one of the powder processing conditions. A further investigation of electron micrographs of the both milled powder was done Figure 5.5 shows the micrographs of MA 2/3 (a) after 45 minutes milling
Figure 5.5. Electron micrographs of MA 2/3 (a) After initial amount of Al (b) After final amount of Al.

with initial amount of Al (b) after final 15 minutes milling and final amount of Al. From (a) and (b) it is clear than not much of the titanium is encapsulated by aluminium. While Figure 5.6 Show the electron micrographs of MA 3/4 (a) after 45 minutes milling with initial amount of Al (b) after final 15 minutes milling and final amount of Al. From Figure 5.6 (a) and (b) it is clear that the amount of titanium encapsulation by aluminium is more as there are very few titanium volume percent in (b). Hence from the Scanning electron micrographs of MA 2/3 and MA 3/4 the powder processing techniques with MA 3/4 looks reliable.

Figure 5.6. Electron micrographs of MA 3/4 (a) After initial amount of Al (b) After final amount of Al.
The total milling time for both MA 2/3 and MA 3/4 is 60 minutes. To ensure that no reaction occurred during milling process inside the vial XRD of the powders was conducted. Figure 5.7 shows the result obtained from the XRD.

![XRD for MA 2/3 and MA 3/4 green compact](image)

**Figure 5.7.** XRD for MA 2/3 and MA 3/4 green compact.

### 5.2 Characterization of Al₃Ti Formed by Combustion Synthesis

During experiment the temperature of the compact was measure via data acquisition system. But none of the temperature profile was repetitive and had a clean curve. So another investigation was done with same MA3/4 powder processing technique just no degassing of powder prior to milling was done and was named MA3/4:1/4. The current applied during the experiment was 550 Amps. Few experiments were done with other current condition too. But none of the temperature profile was reproducible, but a clean curve was produced in one of the experiment it is shown in Figure 5.8. But no further investigation was done on the MA
Figure 5.8. Temperature curve generated by electrical processing of Al₃Ti at 550 amps current condition.

3/4:1/4 sample because the area of interest is with powder processed with Vacuum Degassing with MA 3/4 technique.

As the powder processing technique is decided it is time to decide the current condition. The current used for electrical processing of Al₃Ti (with MA 3/4 powder processing technique) samples are ranging 600 Amps, 800 Amps and 1000 Amps. The reaction is an SHS type of reaction where the ignition typically starts at interface between the electrode and the compact. And it spreads like a wave throughout the specimen. This reaction time is recorded from monitoring the video. Table 5.2 shows the estimated reaction time from the video. From the table it is clear that the reaction time decreases with the increase in the applied current.

Moreover with increase in applied current there also has been increase in the diameter of the corresponding specimen with different rate. Table 5.3 shows the table percentage increase in the diameter of the specimen at different current conditions.
Table 5.2. Ignition Time at Different Current Condition

<table>
<thead>
<tr>
<th>APPLIED CURRENT (A)</th>
<th>IGNITION TIME (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>~18.31</td>
</tr>
<tr>
<td>800</td>
<td>~12.49</td>
</tr>
<tr>
<td>1000</td>
<td>~10.72</td>
</tr>
</tbody>
</table>

Table 5.3. Percentage Increase in Diameter at Different Applied Current

<table>
<thead>
<tr>
<th>APPLIED CURRENT (A)</th>
<th>PERCENTAGE INCREASE IN DIAMETER</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>~11 – 15%</td>
</tr>
<tr>
<td>800</td>
<td>~15 – 31%</td>
</tr>
<tr>
<td>1000</td>
<td>~26 – 36%</td>
</tr>
</tbody>
</table>

For specimens with 600 A current application the electron micrographs are shown in Figure 5.9 where (a) is at low magnification and (b) at high magnification. Due to low heating rate there is more unreacted titanium and aluminium as seen from the micrographs. It is also clearly visible that there very less porosity at 600 A. This image is taken from the center of the specimen.

The Figure 5.10 shows the SEM image of the same specimen (600A) from the top-center region. Both Figure 5.9 (a) and Figure 5.10 looks similar with same amount of porosity and same volume percentage of titanium and aluminium.

Similarly for 800 A the micrographs are shown in Figure 5.11 (a) is at low magnification and (b) at high magnification are taken from the center of the specimen. From the figure you can see that the amount of porosity increases than 600 A. But the amount of unreacted titanium in decreased than 600 A. You can also see more, dark gray phase in the micrographs it has been detected as aluminium by EDS analysis. This means there is more
aluminium present in 800 A than 600 A. But as the 800 A specimen is more porous than the 600 A, we found that while grinding and polishing operation some grain pull out does occur.

Figure 5.12 shows the electron micrograph taken from the top-center region of the same specimen (800A). It can be clearly seen that the amount of aluminium is very less than the amount seen in center of same specimen (Figure 5.11). Also the porosity is much less than the center region of the specimen, the reason for this can be micro cracks formed at the surface of the specimen.

More porosity is observed in the specimen of 1000 A as seen in Figure 5.13. Also during grinding and polishing operations the amount of grain pull out was much higher than that of 800 A. This is the reason why Figure 5.13 (a) does not have high level of accuracy. But from all specimen with different current application 1000 A specimens carries highest porosity which is evident from the all the Figures 5.9, 5.11, and 5.13. While Figure 5.14 is the SEM image of the same specimen (1000A) taken at the top center of the specimen. As seen from the image it is clear that the porosity in less at the top center than the center of the specimen. Also you can see the amount of aluminium is less as compared to center images of all the specimens (600A, 800A, 1000A).
XRD analysis was done on the different specimens for 600 A, 800 A, 1000 A. The XRD plot is shown in Figure 5.15 comparing it with its green compact. The XRD plot reveals that the major intermetallic phase formed during reaction regardless of current condition is Al₃Ti. This means that the combustion synthesis reaction did not take place on micro structural level.

From the XRD you can see that at 600 A and 800 A condition there is residual aluminium in the reacted specimen all the peaks shown in green compact are visible in 600 A and 800 A condition but the peaks are smaller. A similar condition can be seen for titanium in 800 A except there is only few peaks of titanium. But in case of 600 A condition there is more residual titanium, this can be also seen form above micrographs of 600 A, 800 A and 1000 A that more titanium is present in 600A. The XRD plot also reveals that there is some formation of Al₃−Ti at 600 A current. For detail study a table is presented below Table 5.4 stating the amount of aluminium and titanium by tis atomic percentage in the different phase.
seen in the Electron micrographs for 600 A, 800 A and 1000A current processing condition. For 1000 A XRD plot you can see the titanium and aluminium peaks are relatively smaller. So from the SEM images and the XRD plot we can conclude that the amount of titanium decreases and with the increase in current.

In Table 5.4 you can see three different phase color white where amount of titanium is maximum, grey where amount of aluminium is maximum and light grey which is the Al₃Ti intermetallic phase. These quantitative values of the atomic percentage of aluminium and titanium are obtained from the EDS analysis results. It should be mentioned that some inaccuracy may result from data being picked up from neighboring regions of the examined spots, due to the specimen-electron beam interaction volume, which could enter other unintended regions.

While monitoring the video of reaction for all the current condition, it has been noticed that there is some electric sparks in between the tungsten-carbide electrodes and the specimen. It is also revealed that aluminium droplets are formed and travels down the specimen along with some smoke. This smoke is presumed to be aluminium vapor. This can be seen in Figure 5.16. The aluminium droplet appeared as soon as the current application
starts and prior to the combustion synthesis reaction. This formation of droplet is seen in all of the current condition i.e. 600 A, 800 A, 1000 A.

On further investigating the video it is revealed that only the specimen ignited at 1000 A current condition, has a second glow in the central region after the initial glow. From Figure 5.17 we can see that as after the application of current i.e. 1000 A, the specimen starts igniting at and engulfed with the flame within 10 seconds. After the whole specimen is ignited at 16.8 seconds the specimen starts developing a second glow. This glow builds up with time and you can see at 46 second entire center region of the specimen has the glow. This glow remains till the current is flowing. From the electron micrographs and XRD it looks as if there is involvement of titanium and aluminium and their microstructure which contributes to sustain the Joule heating effect to the second glow. The second glow is not only because of the reaction taking place at high current intensity. But the fact that there is an increased amount of porosity and there is more titanium aluminate which has higher
resitivity than aluminium or titanium also plays an important role to develop the second glow.

Figure 5.18 shows the average porosity of the reacted specimen at 600A, 800A and 1000A. The green compact porosity is shown in the figure with a dashed line at 26%. As the applied current density increases the average percentage porosity at the center of the specimen also increases. The average residual porosity of the specimen at 1000 A is maximum at 66%. Due to the high porosity of reacted specimen a lower scale of hardness was selected (HRF). mechanically activated powders for 3 minutes is also similar to the green compact of mechanically activated powders for 60 minutes.

Figure 5.19 show the average hardness of the reacted specimen for 600 A, 800 A and 1000 A. The Rockwell hardness of the center region of the specimen shows that there is slight increase in hardness from 33.2% at 600A to 36.2% this can be possible due to presence of pure titanium in 800 A. As the current applied increases to 1000 A the hardness drastically drops to 17.5 HRF. The average hardness of the unreacted and green compact of 3 minutes milled Al₃Ti is also similar to the green density labeled in the plot.
Figure 5.14. Scanning electron micrograph for 800A at top-center region.
Figure 5.15. XRD of green compact, 600 A, 800 A and 1000 A reacted specimen.
Table 5.4. Table Indicating the Amount of Al and Ti in Different Phase for Current Applied from the Specimen Center

<table>
<thead>
<tr>
<th>Current Applied</th>
<th>White</th>
<th>Light Grey</th>
<th>Grey</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>*Al %</td>
<td>*Ti %</td>
<td>*Al %</td>
</tr>
<tr>
<td>600 A</td>
<td>2.05*</td>
<td>97.95*</td>
<td>76.96*</td>
</tr>
<tr>
<td></td>
<td>1.92</td>
<td>98.08</td>
<td>76.88</td>
</tr>
<tr>
<td></td>
<td>9.59</td>
<td>90.41</td>
<td>76.78</td>
</tr>
<tr>
<td>800 A</td>
<td>5.13*</td>
<td>94.87*</td>
<td>76.64*</td>
</tr>
<tr>
<td></td>
<td>6.64*</td>
<td>93.36*</td>
<td>76.69*</td>
</tr>
<tr>
<td></td>
<td>6.75</td>
<td>93.25</td>
<td>77.26</td>
</tr>
<tr>
<td></td>
<td>1.61</td>
<td>98.39</td>
<td>74.39*</td>
</tr>
<tr>
<td></td>
<td>2.39</td>
<td>97.41</td>
<td>77.47*</td>
</tr>
<tr>
<td></td>
<td>1.53</td>
<td>98.47</td>
<td>78.06*</td>
</tr>
<tr>
<td>1000 A</td>
<td>7.25</td>
<td>92.75</td>
<td>76.13</td>
</tr>
<tr>
<td></td>
<td>20.50</td>
<td>79.50</td>
<td>76.12</td>
</tr>
<tr>
<td></td>
<td>5.75</td>
<td>94.25</td>
<td>75.94*</td>
</tr>
</tbody>
</table>

Note: Table of colors, (*) Indicates the area scan data while the rest of the value indicates point scan data. All the values are in atomic %.
Figure 5.16. Appearance of aluminium droplet and smoke after onset of electric current application.

Figure 5.17. Initial glow and second glow during electric-activated combustion synthesis of Al3Ti at 1000 A current.
Figure 5.18. Average residual porosity of reacted specimen at 600 A, 800 A and 1000 A.

Figure 5.19. Average hardness in HRF of green compact and reacted specimen at 600 A, 800 A and 1000 A.
CHAPTER 6

CONCLUSIONS

The following are the conclusions drawn from the investigation of mechanical and electrical activation on titanium aluminides:

1. At a stage even after milling the Al$_3$+Ti powders for 3 minutes the compact prepared were not able to initiate combustion synthesis reaction at current as high as 1000 A, some samples turned red hot but did not produce Al$_3$Ti intermetallics.

2. Compacts with low current intensity lower that 600 A were found to react but not consistently.

3. For all the electrically processed compacts in order to start an SHS reaction all the elemental powders are required to mechanically milled for an hour.

4. MA 3/4 powder processing technique seems to be reliable and has more encapsulated titanium than the MA 2/3 powder processing technique.

5. As the current intensity increases it has been found that the reaction time where the compact is completely reacted decreases.

6. From the electron micrographs and XRD of all the electrically processed Al$_3$Ti powder compacts, the major phase present is Al$_3$Ti with some titanium and aluminium present as minor phase for 800 A and 1000 A compacts in contrary the minor phase in 600 A compacts is Al$_3$Ti.

7. The 1000 A electrically processed compacts shows complete reaction with the lowest amount of aluminium and titanium phase present of all the other compacts.

8. As the current intensity increases the compact porosity also increases, giving us a highly porous compact around 66% at 1000 A current conditions because the processing is done at low pressure and at this high heating rate the amount of molten aluminium is more than other current conditions.

9. This high level of porosity leads to a drastic drop in the hardness to 17 HRF for 1000 A.
CHAPTER 7

FUTURE SCOPE

Since the investigation for electrically processed SHS of Al₃Ti has some issues to avoid those in future some steps could be useful also some changes can be made to get the desired reaction,

1. Post reaction heat treatments can be used to control the level of porosity and produce homogenized single phase Al₃Ti. These can be done either by prolonging the current application for the 1000A (which experiences a second sustained heating), or by using a furnace as a separate process.

2. Production of Functionally grade materials using the technique.

3. Using nano-structured elemental powders which can be produced after long milling times to enable production of nano-structured Al₃Ti product.

4. Temperature profile can be measured with more sophisticated thermal imaging equipment.
REFERENCES


