

**Protective Coating of Titanium Diboride
Reinforcement Particulates for Improvement of
Titanium Metal Matrix Composite Armor Systems**

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Robert Cody Pack
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ABSTRACT

Titanium and titanium diboride (TiB_2) are two materials that have attracted interest for application in armor systems. Titanium exhibits a high strength-to-weight ratio and good corrosion resistance while TiB_2 exhibits high hardness and stiffness. Combining these into a titanium metal matrix composite would allow the superior ballistic properties to be taken advantage of in one composite material and lead to an improved armor system. The main obstacle behind doing so is the detrimental in situ reaction during processing between the Ti matrix and the TiB_2 reinforcing particles that converts TiB_2 into TiB. It was hypothesized that a protective coating on the TiB_2 particulates would protect and prevent the in situ reaction. Two protective designs were investigated: depositing a carbon layer on the particle surface and also nitrogenizing the particle surface to create a boron nitride (BN) coating. TiB_2 particulates were coated using fluidized bed chemical vapor deposition. Powders were blended and then produced either by pressing and firing or by hot pressing. Three separate experiments were performed: variable time, variable temperature, and hot pressing experiments. Samples were characterized using X-ray diffraction and microscopy focusing on phase identification and the coating's effectiveness in preventing TiB formation. Impact testing using half-size charpy bars cut from the hot pressed plate samples also allowed investigation of impact behavior. The nitrogenizing of the particle surface was shown to be unsuccessful in preventing the conversion of TiB_2 into TiB. Reaction between the Ti matrix and TiB_2 readily occurs if the particles are not coated. The carbon coating was proven successful in preventing the conversion of TiB_2 particles into TiB up to dwell times of 2 h at 1370 °C while also providing complete protection in a sample hot pressed at 1200 °C. The carbon coating design presented was proven successful through a range of processing conditions in preventing the in situ conversion of TiB_2 into TiB providing a route to produce a metal matrix composite wherein the TiB_2 reinforcing particles remain intact and unconverted after processing. This material could lead to the production of an improved armor system.

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CHAPTER 1

INTRODUCTION AND BACKGROUND

Titanium is an intermetallic material that has gained great interest for use in armor applications due to its low density, high strength, and good corrosion properties [1]. Titanium alloy plates have shown promising ballistic properties and have been applied to many current defense systems. Titanium diboride (TiB_2) is a ceramic that has attracted attention for armor applications due to its high hardness and high Young's modulus [2]. Alone, each of these materials shows superior mechanical properties. By combining both Ti and TiB_2 in a metal matrix composite a material could be produced that would take advantage of the superior properties of both materials and ultimately lead to production of a highly successful armor system. A major problem exists though due to the reaction of Ti and TiB_2 during processing that converts the existing TiB_2 into titanium monoboride (TiB). TiB has inferior properties for ballistics when compared to TiB_2 and thus this reaction is a detrimental. It is hypothesized that a protective coating on the TiB_2 particles before processing could protect the particles and eliminate the conversion to TiB and preserve the TiB_2 with its superior properties and lead to an improved armor system.

Titanium Armor History and Overview

Titanium and its alloys have been studied for use in armor applications as early as the 1950's. The first account came in 1950 when Pitler and Hurlich found that titanium alloys performed well as armor against small arms projectiles [3, 4]. Later in the early 1960's, Silney demonstrated significant weight reductions over existing steel armors for small arms projectiles using the Ti-6Al-4V alloy [4-6]. By 1964, ballistic testing had shown that by reducing the interstitial elements of carbon, oxygen, nitrogen, and hydrogen, the ductility was improved leading to better ballistic protection of the plate. Thus, extra low interstitial (ELI) grade Ti-6Al-4V became the material choice for armor applications. Even though early investigations showed promise of using titanium and its alloys, especially Ti-6Al-4V, to reduce weight and improve armor systems, applications were restricted to small arms threats due to the high cost of titanium [7]. Through the 1960's and 1970's, a large amount of data was collected on titanium armor and its ballistic properties but it was primarily against smaller caliber projectiles [8]. More recently in the 1990's, interest in titanium armor applications lead to research that showed titanium's ballistic performance against numerous projectiles [5].

Titanium and its alloys are advantageous for armor applications due to their high mass efficiency, high strength-to-weight ratios, and excellent corrosion resistance. A high strength-to-weight ratio allows Ti to have a higher mass efficiency (E_m) defined as the weight per unit area of rolled homogenous steel armor (RHA) required to stop a certain ballistic or projectile divided by the weight

per unit area of a given material [8]. The RHA value is utilized as the baseline for comparing mostly all ballistic materials with an E_m of 1. In comparison, Ti has an E_m of 1.3 to 1.7 over a wide range of threats making it an interesting alternative since most alternative materials do not exhibit this behavior [5]. For example, some materials will exhibit a higher E_m for one type of projectile but will exhibit a lower E_m for a different type of projectile. A higher E_m allows a smaller amount of armor to be used resulting in a lighter overall weight to achieve ballistic protection over the wide range of threats.

Weight reduction has played a key role in the increasing use of titanium alloys in armor systems. It is estimated that a 30-40% weight reduction on vehicles can be achieved when replacing RHA with Ti-6Al-4V armor while still retaining survivability [9]. As warfare has changed, so have the armoring concepts and the need for lighter armor and a potential application for titanium armor systems was demonstrated recently in Iraq where the harsh terrain prompted the need for light and agile armored, support, and tactical vehicles. However, the guerrilla style warfare has invoked the need for ballistic protection from 360-degree threats such as rocket propelled grenades and improvised explosive devices. These lighter vehicles have smaller power trains and chassis that require a lighter armor that will not overload them to protect against these threats [10].

Titanium armor has been applied to several current applications and has demonstrated success. The M1A2 Abrams battle tank utilizes titanium armor in the commander's hatch, internal armor, and armor skirts. The M2 Bradley fighting vehicle uses it in the commander's hatch while titanium roof armor is added for increased protection. In the Stryker family of vehicles, titanium has replaced steel armor in many applications such as the gunner's protection kit on various models [5, 10].

Although monolithic titanium armor systems have proved successful in many ballistic applications because of their high mass efficiency, high strength-to-weight ratio, and excellent corrosion resistance, improvements can still be made. The development of a titanium/ceramic composite could take advantage of the superior properties of each material to produce an even higher performance armor material.

Ceramic Armor History and Overview

Ceramic materials garnered attention for use in armor systems for many years due to their high hardness, high elastic modulus, and high ballistic resistance. It was first observed that ceramics provided ballistic protection in 1918 when it was shown that a hard enamel coating on steel provided increased resistance to bullets [2, 11]. The earliest ceramic armors consisted of alumina plates attached to a woven backing. In 1963 the Goodyear Aerospace Company was awarded the first patented ceramic armor [12]. Later in the 1960's, Norton Ceramics developed boron carbide (B_4C) plates in an attempt to decrease

weight. This technology led to boron carbide plates on woven backings being used in personal protective vests, which became the first major U.S. ground force use of ceramic composite armor. This same ceramic armor technology was used in 1969 for the first ballistic helicopter seat in the Cobra helicopter [12].

These early innovations set the foundation for the use of ceramics in armor systems. After 1970, armor production slowed but interest in ceramic armor technology continued to increase [12]. Many discoveries and improvements have been made since then ranging from different ceramic armor designs and configurations to greatly improved testing abilities that have allowed the detailed studies of ceramic armor behavior.

Currently, ceramic armor has a firm place in armor applications. Solid alumina became a mainstay where it was widely used in numerous personnel armor systems due to its low cost and low density when compared to metals. However, additional alumina had to be added due to the danger from increasingly lethal threats over time causing alumina armor systems to suffer from increasing weight. Thus, silicon carbide (SiC) and boron carbide (B_4C) became more commonly used [13]. B_4C is now predominantly used in personal armor vests for personal protection as well as other applications such as in seats in armored land vehicles while SiC is usually used in armored vehicles as add on armor for protection against larger caliber threats such as machine gun fire and medium cannon threats [14]. TiB_2 has not been extensively used in common armor systems even though it possesses superior properties and has been proven to successfully perform in ballistic protection. This is mainly due to its lack of alternative market applications [14], however, interest in the application of TiB_2 for ballistic protection remains great, leaving the door open for the production of an improved armor system.

Particulate Reinforced Metal Matrix Composites (PMMCs)

While titanium and ceramic armor systems alone have been utilized greatly and shown to perform successfully, each system has drawbacks. Composite systems that incorporate both metals and ceramics offer a way to overcome the disadvantages of the standalone systems and produce an overall improved armor system. Composites allow the unique benefit of being able to combine advantageous properties of two different materials into one composite material. By definition, a composite is considered to be any multiphase material that exhibits a significant proportion of the properties of the constituent phases such that a better combination of properties is realized [15]. Two-phase systems are made up of a continuous matrix surrounding a second dispersed phase and the overall properties of the composite are a function of the properties of the constituent phases, their relative amounts, and the geometry of the dispersed phase [15].

Many different types and designs of metal/ceramic composite systems

exist, however this study focuses on development of a Particulate reinforced Metal Matrix Composite (PMMC) for application in Functionally Graded Armor Composites (FGAC). PMMCs are fitting for armor applications due to the combined metallic properties of ductility and toughness with the ceramic properties of hardness, stiffness, and strength [16]. They can be divided into two types: continuous reinforced composites with fibers or wires and discontinuous reinforced composites. Continuous reinforced composites have shown promise in producing high performance composites but they are extremely difficult and laborious to produce leading to high production costs. Their production is plagued with additional problems such as reinforcement damage and non-uniform structure [16]. Discontinuous reinforced composites can encompass short fibers, whiskers, and particulates [16, 17].

More specifically, PMMCs consist of ceramic reinforcing particles greater than 1 μm in diameter dispersed within a metal matrix [18]. The reinforcing particulates act to harden and stiffen the composite while the metal matrix provides ductility and strength. PMMCs attract attention over continuously reinforced composites due to the availability of reinforcement phases at a lower cost and the easier manufacturing through use of powder metallurgy and hot pressing. PMMCs attract interest for armor applications due to their tailorability to acquire the desired combined properties. Ideally, a lightweight, ductile, and tough metal matrix can be reinforced with stiff, hard, and strong ceramic particulates to create an overall composite armor material capable of successful projectile defeat.

Functionally Graded Armor Composites (FGAC)

PMMC's are advantageous for use in FGAC technologies. Functionally graded materials by definition are advanced composites whose properties vary continuously through a given dimension [19]. This variation in properties can be achieved by varying the volume ratio of the reinforcing particles in PMMCs allowing for the production of a material combining the protective performance of ceramics with the strength of metals where the optimum combination of hardness and ductility is achieved in specific locations of the armor [20]. A design consisting of a harder frontal area and a softer backing area is intended to defeat a light to medium projectile. The hard front acts to blunt and/or erode the projectile while the softer backing acts to "catch" the broken projectile fragments preventing penetration [21, 22]. In such a design the front contains a higher volume fraction of the ceramic reinforcement particles creating the harder material and the backing area contains a smaller volume fraction of the ceramic reinforcement particles and a corresponding larger volume fraction of the metal matrix creating the more ductile material. In between the two extreme faces, the composition can be varied to obtain the desired properties as shown in Figure 1. Ease of production can be realized through use of powder metallurgy technology

and hot pressing by loading the die with different volume fractions of powdered matrix metal and ceramic reinforcing particulates.



Figure 1. Cross-section of a FGAC. Adapted from [20] illustrating the variation in properties from the hard front region to back ductile region achievable through PMMC technology.

PMMC and FGAC Design and Materials Selection

Overall, improvements in high performance projectiles and their increased use constitute a growing threat that calls for development of new lightweight armor systems. This need could be met by design and development of FGAC fabricated from PMMCs. Selection of matrix and reinforcement materials is essential in designing an effective and efficient FGAC. While selection based on material properties important to ballistics will be discussed in the next section, additional properties must be considered. PMMC processing, which involves heating the material up to elevated temperatures followed by cooling down to room temperature, introduces thermochemical and thermomechanical issues, therefore thermochemical and thermomechanical stability are two of the main factors that must be considered in design and selection. In order to produce a successful FGAC, the composite must be mechanically stable after manufacturing. To achieve this, it is desirable that the thermal expansion coefficients of the constituents are similar [20]. Large differences in the expansion and contraction of the constituents upon heating and cooling result in large residual stresses remaining in the final product and possible pore formation inhibiting the armor's ability to absorb energy from projectile impact and successfully defeat the projectile.

To take advantage of combining the benefits of the metal and ceramic constituents thermochemical stability must be achieved. Some matrix–reinforcement combinations can be highly reactive with each other at elevated temperatures [15] and consequently, chemical reactions will lead to the matrix degrading or “chewing” up the particles or to particulate transformation from a desired compound with superior properties to an undesired compound with inferior properties and ultimately deteriorate the performance of the composite. Possible solutions to prevent this are modifying the matrix composition with non-reactive elements or coating the particles to protect them.

Material Properties Important to Ballistic Performance

At the current time, armor performance has not been correlated to a single material property. This is due to the dynamic nature of ballistic events which occur in nano to micro seconds producing extremely high strain rates [20]. However, there are some certain material properties for material selection and design that have been shown to have an influence on the success of an armor system.

The metal matrix material serves as a compliant support and must possess good ductility yet be strong enough to capture the projectile fragments. Ductility and strength also contribute to the armors multi-hit resistance. Density of the constituent is directly related to the overall weight of the armor and ideally, a matrix with a high strength to weight ratio is desired.

The reinforcement particulate material in PMMCs is the stiffer, harder material. While no specific material property can be used to predict an armor's performance, hardness, strength, density, elastic modulus, and fracture toughness have been shown to have an influence on a ceramic's ballistic performance and are several key properties that can be used to guide design for armors that will defeat projectiles. Woodward and Baxter determined that by blunting a projectile, its ability to penetrate through the backing is decreased [13]. If a ceramic has a high enough hardness, it can blunt, erode, or destroy the projectile and thus increase the ballistic performance [23]. Shockey et al. determined that the compressive strength of a ceramic determines its initial resistance to a projectile and can result in cracking, deforming, or deflecting the projectile tip depending on the compressive strength [2, 24]. Analogous to the matrix material, a lower density particulate material is beneficial for an overall lighter weight armor system. The elastic modulus plays a role in a ceramic's stiffness and ability to resist deformation to failure and a higher modulus provides a better probability of defeating a projectile [11]. Fracture toughness has an influence on the ballistic performance of a ceramic although the process is not fully understood. Generally high fracture toughness is desired to obtain multi-hit capability and durability [25]. However, a high fracture toughness is not a guarantee for good performance since some ceramics exhibit a high fracture toughness yet do not show good protection capabilities [13]. Overall, the superior ballistic ceramics have a high hardness, elastic modulus, and fracture toughness combined with a low density for lighter weight.

Titanium Diboride Background and Properties

Titanium diboride (TiB_2) is a ceramic with current applications in wear resistant coatings, armor, cutting tools and crucibles. Ceramics are compounds formed from a combination of metallic and nonmetallic elements that are generally hard and stiff and melt at high temperatures. These properties are due to the strong covalent/ionic bonding between the elements [2]. TiB_2 is a stable compound between titanium and boron as can be seen in the Ti-B phase diagram in Figure 2 [26]. It is a solid solution that exists over a stoichiometric range of 30.1-31.1 wt% B and has a congruent melting point at 3225°C. TiB_2 exhibits hexagonal symmetry with the Ti atoms at (0,0,0) and B atoms at $(1/3, 2/3, 1/2)$ and $(2/3, 1/3, 1/2)$ lattice sites [15].

TiB_2 possesses many superior mechanical properties that make it a favorable candidate for armor applications and Table 1 compares the mechanical properties of common ballistic ceramic reinforcements [16, 27-29]. Notably, TiB_2 has an extremely high hardness of 25-30 GPa at room temperature and retains it to high temperatures. It is the second hardest common ballistic ceramic, only inferior to boron carbide (B_4C). TiB_2 is the stiffest reinforcement with the highest Young's modulus of 541-575 GPa.

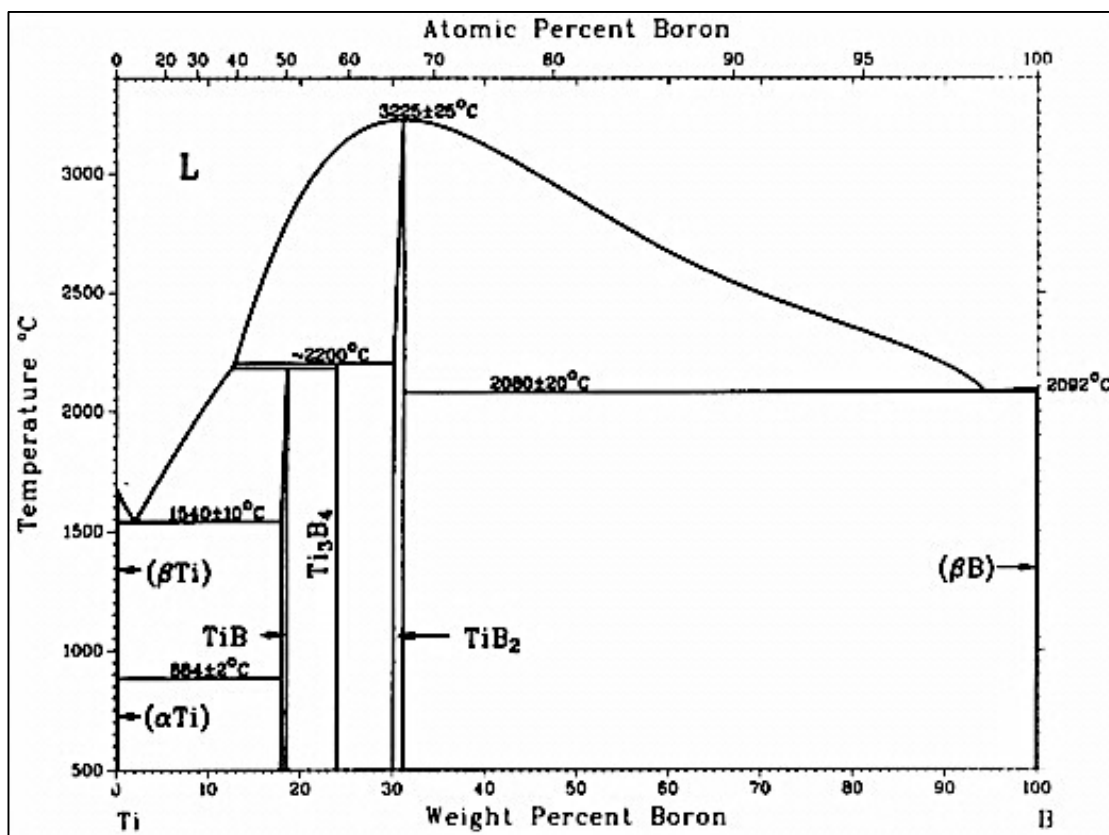


Figure 2. Ti-B binary phase diagram. From [26].

Table 1. Physical, mechanical, and thermal properties of common ballistic ceramic reinforcements.
Sources [16, 27-29].

Compound	Density (g/cm ³)	Young's Modulus E (GPa)	Vicker's Hardness (GPa)	Compressive Strength (GPa)	Coefficient of Thermal Expansion (10 ⁻⁶ /C)	Fracture Toughness K (MPa-m ^{1/2})
Sic, hot pressed	3.09-3.2	380-440	20	3.41	5.4	5-5.5
Al ₂ O ₃ , sintered	3.6-3.95	300-450	13-18	2.6-3.1	7.92	3.0-4.5
B ₄ C, hot pressed	2.49- 2.51	432-450	29-35	4.5-6	6.08	2.5-3.1
TiB ₂ , hot pressed	4.43- 4.51	541-575	25-30	4.8-5.7	7.4-9.8	6.7-6.95
TiB	4.54-4.6	427-450	18.6-19	--	7.15-11.3	4.5-5.5
TiC	4.93	380-440	29-32	2.5	7.6	3.8

TiB₂ also exhibits the highest fracture toughness with 6.7-6.95 MPa-m^{1/2}, however, one limitation is the high density when compared to other ballistic ceramics. This slightly hinders the lightweight ability and results in TiB₂ being more widely used in a composite rather than a monolithic system [26].

Titanium Background and Properties

Titanium is a transition metal that exists in two crystallographic forms known as α and β . α refers to hexagonal close packed (hcp) Ti while β refers to body-centered cubic (bcc) Ti. Pure, unalloyed Ti will be α from room temperature up to 884 °C (Figure 2) and above 884 °C transforms to the β phase remaining stable up to the melting point which is in excess of 1660 °C [2]. By adding alloying elements to pure Ti, the transformation temperatures and the amount of each phase present can be varied and certain elements can be used to stabilize the α phase while other ones can be used to stabilize the β phase. Numerous alloys have been developed utilizing various alloying elements but only commercially pure titanium (CP-Ti) and Ti-6Al-4V will be discussed since they are relevant to the this study. Ti-6Al-4V is an alloy consisting of 6 wt% Al and 4 wt% V where the Al stabilizes the α phase to higher temperatures while the V stabilizes the β phase to lower temperatures. Thus Ti-6Al-4V is an alpha-beta alloy able to be heat-treated for providing a combination of strength and ductility attractive for armor applications [30]. α -Ti is superior in its corrosion resistance, ductility, and weldability to Ti-6Al-4V but has a lower strength. Table 2 compares some of the material properties of CP-Ti and Ti-6Al-4V.

Table 2. Physical, mechanical, and thermal properties of CP-Ti and Ti-6Al-4V. From [30].

	Density (g/cm ³)	Tensile Strength (MPa)	Coefficient of Thermal Expansion (10 ⁻⁶ /C)	Charpy Impact Strength (ft-lbf)	Young's Modulus E (GPa)	Fracture Toughness (MPa-m ^{1/2})
CP-Ti	4.5	500-640	8.6-9.7	20-26	93-120	85
Ti-6Al-4V	4.43	850-1000	8.6-9.7	20-24	114	83-100

Reaction of TiB₂ with Ti During Processing

Reinforcement particles and the metal matrix can be highly reactive with each other when heated to high temperatures such as those experienced during processing. The phase diagram in Figure 2 shows the compounds TiB, Ti₃B₄, and TiB₂ that form at 18-18.5 wt%, 22.4 wt%, and 30.1-31.1 wt% B, respectively. TiB and TiB₂ are stable compounds that exist in the Ti-B system while Ti₃B₄ has been shown to be metastable. Madtha et al. [29] did not report evidence of the intermediate compound Ti₃B₄ during reactions between Ti and TiB₂ from hot pressing. The formation of TiB through the reaction of Ti with TiB₂ is the pertinent problem and will be the focus while the Ti₃B₄ formation will not be addressed. The Ti matrix reacts with the TiB₂ particles according to equation 1.



This reaction is further understood through thermodynamic evaluation. Panda and Chandran [31] calculated the free energy of formation for the reaction using standard thermodynamic data. Figure 3 illustrates that the reaction is possible and thermodynamically favorable due to the small negative free energy (G) at higher temperatures supporting that during processing, TiB forms by using TiB₂ as a boron source and reacting with the Ti matrix [29]. As in this study, if temperatures remain below the solidus line then the above reaction proceeds as a solid-state reaction driven by the diffusion of B into the Ti matrix [32, 33].

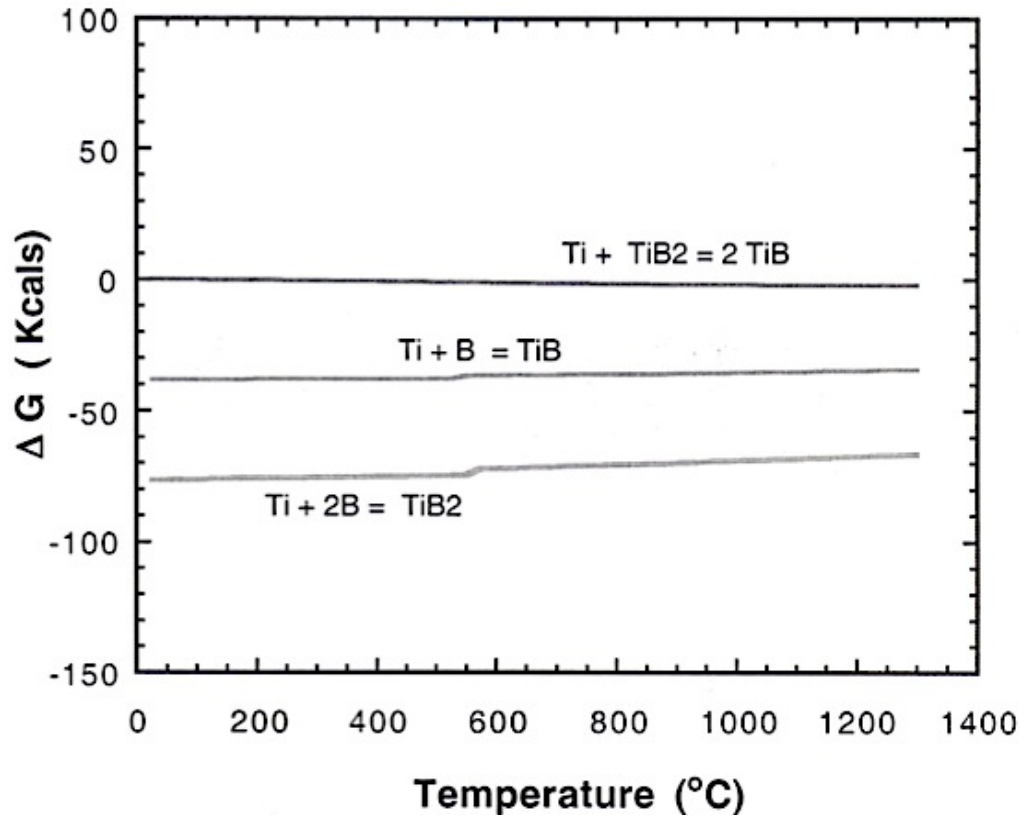


Figure 3. Free energy diagram for TiB and TiB₂ formation. Note that the change in free energy (G) of the top reaction becomes slightly negative at higher temperatures. From [31].

While this reaction is detrimental for developing superior armor, a few researchers have taken advantage of it for production of TiB through reaction sintering. Panda and Chandran [31] produced Ti-TiB composites with varying volume fractions of TiB by hot pressing Ti and TiB₂ powders. These composites were hot pressed at temperatures from 1100-1300 $^{\circ}\text{C}$ for 2 h at 28 MPa. Madtha et al. [29] synthesized nearly 100% monolithic TiB by a similar process of hot pressing Ti and TiB₂ powders under an inert Ar atmosphere at approximately 1300 $^{\circ}\text{C}$ and 10-15 MPa. Sahay et al. [34] fabricated various volume fractions of TiB by hot pressing Ti and TiB₂ powders. In all the composites, TiB was the predominant boride phase containing a small volume of unreacted TiB₂ and no evidence of Ti₃B₄. These studies had a different focus than the present study due to their desired conversion of TiB₂ into TiB, however, they demonstrated that the reaction of Ti with TiB₂ does readily occur during processing leading to the depletion of TiB₂ and the formation of TiB.

Further studies, specific to Ti-TiB₂ FGAC also demonstrate the occurrence of TiB formation. Gooch and Burkins [33] developed and tested a functionally

graded armor wherein Ti and TiB_2 powders were hot pressed to form a graded Ti-TiB armor and TiB formation was observed beforehand and accounted for in the design of the armor. Another study by Pettersson et al. [20] attempted to produce a Ti- TiB_2 graded armor system through spark plasma sintering where spark plasma sintering is similar to conventional hot pressing, however, it enables faster heating and cooling rates resulting in shorter processing times. Even with the rapid process, the in situ reaction was shown to take place with formation of fine TiB whiskers. These studies prompted recognition that a negative aspect was the formation of TiB during processing.

In order to develop a superior armor system that is capable of combining the beneficial properties of both Ti and TiB_2 , the in situ conversion of TiB_2 to TiB must be eliminated. The main goal of the present study was to investigate and eliminate this detrimental reaction that has been shown by numerous studies to readily occur during processing. Since Ti and TiB_2 are highly reactive at the elevated temperatures during processing, a procedure to produce a protective coating on the reinforcing particles was devised and investigated.

CHAPTER 2 EXPERIMENTAL

Materials

The commercially pure titanium (CP-Ti) powder was produced by International Titanium Powder (ITP) and TiB₂ particulate powder was obtained from ESK Ceramics in +50 µm sizing.

Powder Processes

Sieving of TiB₂ Powder

In order to obtain the desired particulates of greater than 50 µm diameter the powder had to be further size filtered by starting with 100 g of powder in a +53 µm sieve on a vibrating sieve stand and allowing it to run for 0.5 h. The powder that did not filter through the sieve was subsequently collected. Three 100 g starting batches were used for producing 150 g of sieved powder. To further refine the particle size the 150 g of +53 µm powder was sieved once more for 0.5 h and the remaining powder was collected, stored, and used in the following experiments.

Milling of ITP CP-Ti Powder

The as received CP-Ti powder was unmilled and in order to improve the handling 1300 g of CP-Ti powder was ball milled in ethanol with zirconia milling media for 0.75 h.

Powder Blending

In order to form a metal matrix composite, the reinforcing particulates have to be evenly dispersed within the powder mass before processing. The ball milled CP-Ti powder was used through this whole study as the metal matrix component. The reinforcement particles consisted of uncoated (TB), carbon coated (C), and nitrogenized (N) TiB₂ particles. To blend the CP-Ti powder with the reinforcing particles, the CP-Ti powder was mixed with 10 volume% reinforcing particles. Cylindrical blending media were used to aid the blending. Each blending bottle contained approximately 350 g of total powder resulting in the bottle being less than half full. Once the powder was placed in the bottle, the lid was secured and bottle was placed on mill rollers allowing the contents inside to blend. Rolling speed was set by visual observations and was intended to accomplish frequent powder overturn without resulting in the powder climbing up the walls of the bottle and free falling back to the bottom. In this manner the powders were blended for 24 h to achieve uniform dispersion of reinforcing particles within the metal powder. Once blended, the powders were used for subsequent processing such as consolidating and firing or hot pressing.

Coating of TiB₂ Particles

The goal of this study was to produce a protective coating on the reinforcing particulates to inhibit the detrimental reaction of the Ti matrix with the TiB₂ particles. Both deposition of a carbon coating and nitrogenizing of the TiB₂ surface to produce a boron nitride (BN) coating using chemical vapor deposition (CVD), were initially investigated. Fluidized Bed CVD (FBCVD) was chosen due to its ability to produce a full and uniform coating.

FBCVD System

The FBCVD system was configured so that the both the reactant and inert gases could be introduced into the furnace. The system was comprised of a furnace with a gas injector connected to a conical shaped graphite-coating chamber. The coating chamber or cone is surrounded by a graphite-heating element and enclosed in a water-cooled shell. The gases, both reactant and inert, are introduced into the bottom of the cone through the injector. The gas fluidizes the particles and coats them inside the cone and then exits through an exhaust port at the top of the furnace. Figure 4 illustrates the gas injector and fluidized bed in the graphite-coating chamber. The temperature of the fluidized bed was measured using a hand-help optical pyrometer looking through the sight glass at the top of the furnace. Figure 5 illustrates a complete FBCVD system showing all of the components and their locations.

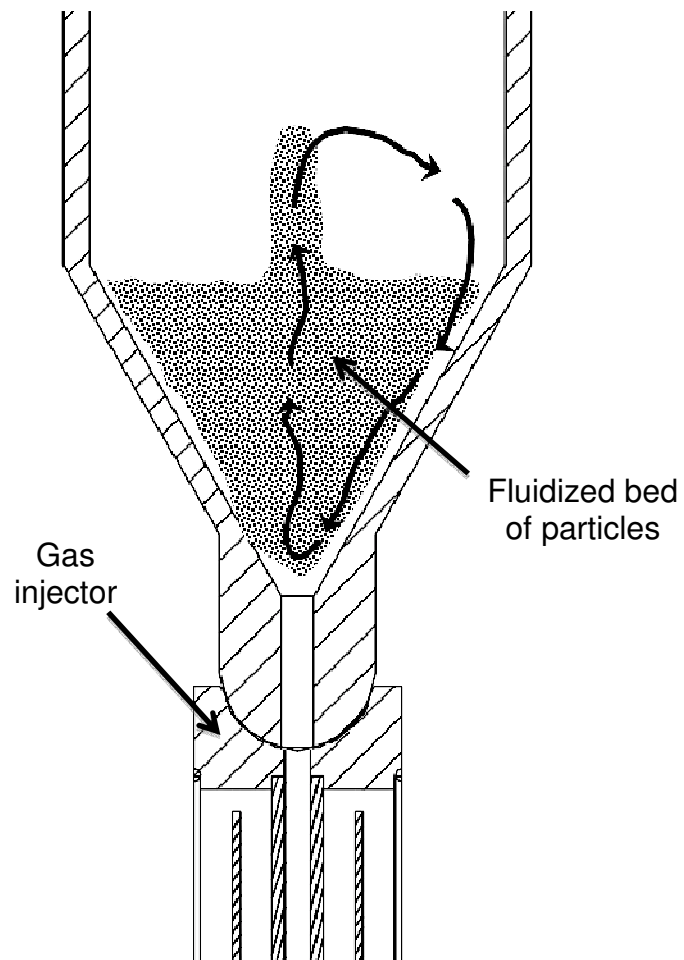


Figure 4. Enlarged depiction of gas injector, fluidized bed, and graphite cone.

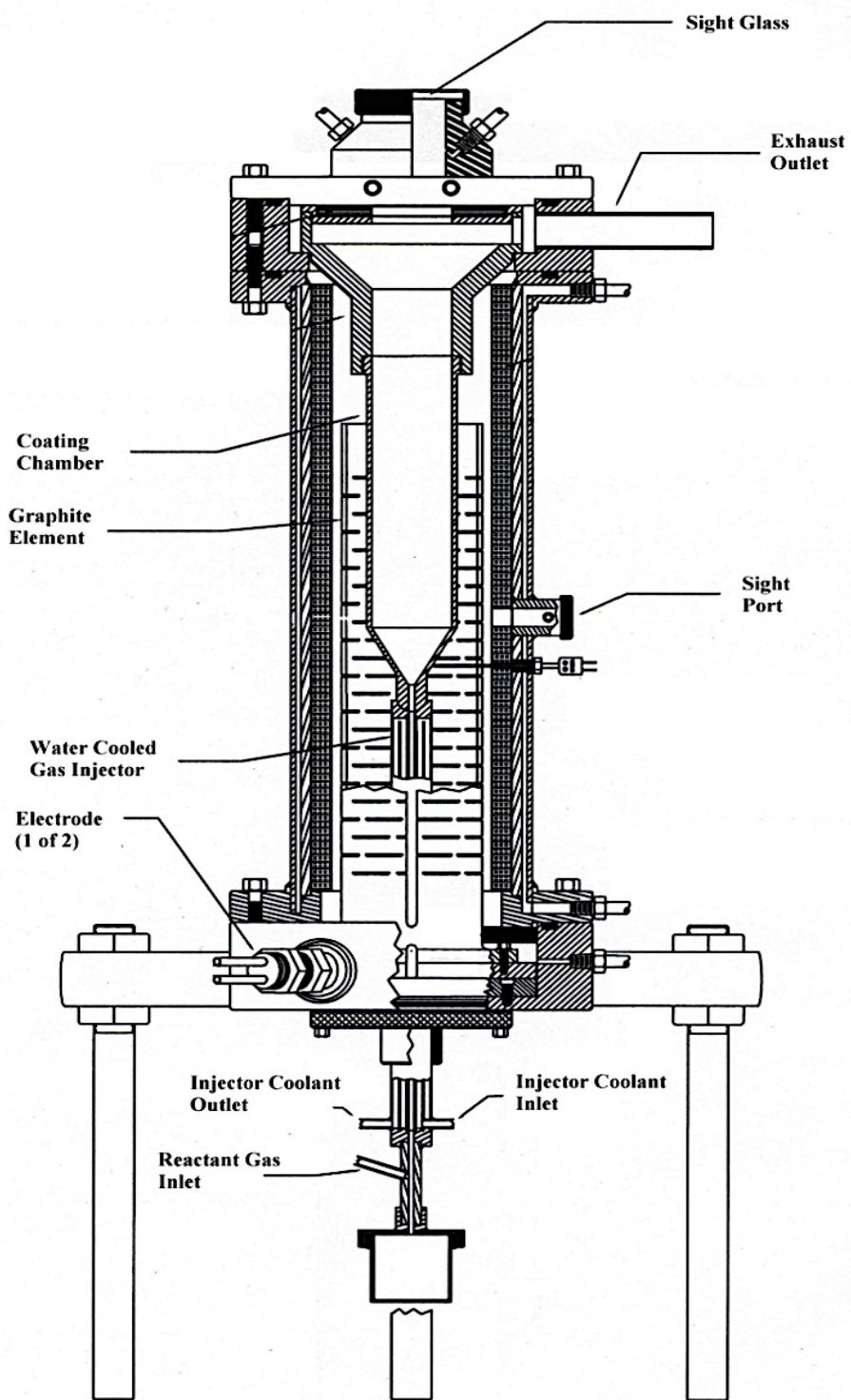


Figure 5. Cutaway of a CVD Reactor

Coating Procedure

Coating of the TiB_2 particles was achieved by loading the particles into the furnace under inert gas flow in order to fluidize the particles and then raising the temperature to a determined reaction temperature. The reactant gases were then introduced at a desired flow rate. The flow rate and temperature were maintained for a desired time period after which the reactant gas flow was terminated and the temperature lowered back to room temperature and the particles unloaded.

Argon (Ar) was used as the inert gas in the carbon and nitrogen coating studies. Initially, 11 g of the $+53\ \mu\text{m}$ TiB_2 particles were mixed with 4 g of $300\ \mu\text{m}$ zirconium dioxide (ZrO_2) spheres. The ZrO_2 spheres were used to mix up and fluidize the particles. The particles were then loaded into the furnace through a funnel in the top sight glass port while Ar gas was flowing. The temperature of the furnace was raised to the desired temperature and monitored using a hand-help optical pyrometer looking through the sight glass at the top of the furnace. Once the target temperature was achieved, a flow rate of Ar and reactant gases was established. The fluidizing Ar flow was then routed to the exhaust bypassing the furnace while the Ar/reactant gas mixture was directed into the cone initiating the coating. The coating process continued for a determined time period at the desired temperature. Once the target time was achieved the Ar/reactant gas was diverted from the cone while the inert Ar gas was diverted back into the cone. Then the heating element was powered off allowing it to cool back to room temperature and once at room temperature, the fluidizing Ar gas was shut off allowing the particles to fall out the bottom into a container.

Once all the particles had settled out of the bottom, the coated TiB_2 particles had to be separated from the ZrO_2 spheres by simple size exclusion through sieving. The particles were poured on top of a $180\text{-}\mu\text{m}$ sieve and lightly shaken and the coated TiB_2 particles easily passed through the mesh into the bottom catch pan while the ZrO_2 spheres remained on top of the sieve. The ZrO_2 spheres were disposed of and the coated TiB_2 particles were saved for further experiments.

Table 3 compares the parameters used for the different coating types.

Table 3. FBCVD coating parameters.

	Gas Flow (l/mi)				
Coating	Argon (Ar)	Acetylene (C_2H_2)	Propylene (C_3H_6)	Nitrogen (N_2)	Run Time (Min)
Carbon	0.53	0.122	0.103	0.0	14
Nitrogen	0.55	N/A	N/A	0.2	6

Consolidation and Firing

Four different types of discs were produced from powders: plain CP-Ti (Ti), CP-Ti/uncoated TiB₂ (TB), CP-Ti/ carbon coated TiB₂ (C), and CP-Ti/ nitrogenized TiB₂ (N). These discs were produced by consolidation using a hydraulic press followed by firing in a BREW furnace. Table 4 summarizes the different sample types, their composition and the symbol notation.

Table 4. Sample compositions and notations.

<u>Sample</u>	<u>Composition by Volume</u>	<u>Notation</u>
CP-Ti	100% CP-Ti	Ti
CP-Ti/ uncoated TiB ₂	90% CP Ti / 10% TiB ₂	TB
CP-Ti/ carbon coated TiB ₂	90% CP-Ti/ 10% C coated TiB ₂	C
CP-Ti/ nitrogen coated TiB ₂	90% CP-Ti/ 10% N coated TiB ₂	N

Consolidation

The pure CP-Ti (Ti) and the three composites (TB, C, and N) were blended as described earlier to achieve powders with 10 vol% reinforcing TiB₂ particles and subsequently consolidated into discs. Ten discs were pressed for each of the four sample types resulting in a total of 40 discs.

A hydraulic press and 1.27 cm diameter steel die was used to produce discs with a diameter of 1.27 cm and height of 0.3175 cm. The inside of the die was coated with stearic acid in acetone to provide lubrication. Using the theoretical density and desired volume it was calculated that 1.8 g of powder was needed for discs with the above dimensions. The 1.8 g of powder was then poured into the die and the die assembly was placed and secured in the press. The press was initiated and held at 75 Ksi for 3 s before releasing. After releasing the discs were removed and stored for firing.

Firing of Discs

Once pressed, the discs were then fired under vacuum and heated to the target temperature at a rate of 5°C/min in a BREW furnace. Firing parameters that varied were the hold temperatures and dwell times.

A sample of each type, for a total of four discs/sample boat, were loaded in the furnace with the lid shut and secured. The furnace chamber was then pumped down and back filled with Ar twice and after these two cycles, the chamber was once again pumped down to vacuum and once at vacuum, the controller was set for the desired hold temperature and dwell time and the firing initiated. Once the specified dwell time was reached the firing procedure was considered completed and the discs were removed for further characterization.

Constant Temperature/Variable Time Experiments

Initial experiments conducted to vary the time at which the composites were held at 1370 °C during firing. This was performed to investigate if the coatings would protect the TiB₂ particles from reaction with the matrix and if so, to determine the time it would take for the coating to be completely consumed by the matrix. Five different dwell times at 1370 °C were investigated: 0.5, 1, 2, and 5 h. Table 5 shows the different sample notation and dwell times.

Table 5. Sample notation and dwell times for samples fired at 1370 °C.

Sample Notation	Dwell Time (h)
Ti-30	0.5
TB-30	0.5
C-30	0.5
N-30	0.5
Ti-1	1
TB-1	1
C-1	1
N-1	1
Ti-2	2
TB-2	2
C-2	2
N-2	2
Ti-5	5
TB-5	5
C-5	5
N-5	5

Constant Time/Variable Temperature Experiments

After investigating dwell times, firing temperature was investigated using a constant dwell time of 0.5 h and firing at either 900, 1000, 1100, 1200, or 1300 °C. Table 6 shows the different sample notations and firing temperatures.

Table 6. Sample notation and firing temperature for samples held at temperature for 0.5 h.

Sample Notation	Firing Temperature °C
Ti-6	900
TB-6	900
C-6	900
Ti-7	1000
TB-7	1000
C-7	1000
Ti-8	1100
TB-8	1100
C-8	1100
Ti-9	1200
TB-9	1200
C-9	1200
Ti-10	1300
TB-10	1300
C-10	1300

Hot Pressing Procedures

Hot pressing experiments were conducted to test the carbon coating's protective ability under the processing conditions of combined high temperatures and pressure. Samples produced in this study were later used for impact testing of the composites.

Hot Pressing

Three 5.08 x 5.08 x 0.635 cm plates were processed in an indirect resistance heating hot press. Using the theoretical density for CP-Ti (4.5 g/cm³) and desired volume it was calculated that 75 g of powder was needed for plates with the above dimensions. A square 5.08 x 5.08 cm channel die, where the inside of the die was lined with graphite foil to prevent reaction of the die with the powders, was used to consolidate the powders. Once lined, the die was filled with the specific previously blended powder (Ti, TB, C), loaded into the hot press and then the hot press chamber was evacuated and backfilled with N₂ gas then evacuated one final time. After initiating power to the hot press and heating elements, the controller was programmed and the program started. Each plate was held at temperature for 0.5 h under 3 Ksi (20.68 MPa) pressure. The pure CP-Ti plate (Ti) was pressed at approximately 1100 °C while the composite plates (TB, C) were pressed at approximately 1200 °C. The press was then allowed to cool back to room temperature and the die removed. The plate was then extracted and lightly ground to remove remnants of graphite foil. Table 7 summarizes the hot pressing parameters for the three plates.

Table 7. Hot pressing parameters.

Sample Plate	Composition (wt%)	Pressing Temperature (°C)	Hold Time (h)	Pressure (Ksi)
Ti	100% CP-Ti	1111	0.5	3
TB	90% CP-Ti 10% TiB ₂	1190	0.5	3
C	90% CP-Ti 10% Carbon coated TiB ₂	1195	0.5	3

Characterization Techniques

X-Ray Diffraction

X-ray Diffraction (XRD) characterization was utilized for phase identification as a way of evaluating the effectiveness of the coatings. Continuous Θ – 2Θ scans were performed on a PANalytical XPert MPD diffractometer from nominally 8 to $80^\circ 2\theta$ and total data collection time was 1 h using the X'Celerator detector. Data were collected on samples generated from the variable time/constant temperature and hot pressing syntheses using $\text{CuK}\alpha$ radiation ($\lambda=1.540598 \text{ \AA}$) while data were collected on samples generated from the constant time/variable temperature syntheses using $\text{MoK}\alpha$ radiation ($\lambda=0.70930 \text{ \AA}$). The software packages Jade (MDI software) [35] and HighScore (PANalytical) [36] both interfaced to the International Centre for Diffraction Data (ICDD) database were used for phase identification.

Microscopy

A Nikon labophot 2 optical microscope was used to image mounted and polished samples, at magnifications of 100 and 400 X, generated from the variable time/constant temperature syntheses while a Leica DMI 5000 M Metallograph Microscope was used for the samples generated from the hot pressing syntheses.

A Hitachi S4800 Scanning Electron Microscope (SEM) was used to image mounted and polished samples, at magnifications of 500 – 2000 x using a voltage of 15 Kv, generated from the constant time/variable firing temperature syntheses.

Impact Testing

To test the impact behavior of the samples generated using the hot pressing technique, $\frac{1}{2}$ size charpy bars were cut from the hot pressed plates. The use of the $\frac{1}{2}$ size bars was due to the smaller $5.08 \times 5.08 \times 0.635 \text{ cm}$ size of the plates. Five bars were cut from each plate using electrical discharge machining (EDM). Once cut, the bars were tested using a conventional impact tester with specialized sample holders and indenters for the $\frac{1}{2}$ size bar.

CHAPTER 3

RESULTS AND DISCUSSION

The main goal was to form a protective coating on the reinforcing TiB_2 particles in a titanium metal matrix composite, preventing TiB_2 conversion into TiB following Equation 1. Experiments were aimed at determining whether or not the coating was successful at preventing the reaction and secondarily investigating the behavior of the coating. The following presents the results that were obtained.

Variable Time/Constant Temperature

XRD Characterization

XRD data collected on samples of the pure CP-Ti (Ti) that were fired at 1370°C and held for either 0.5, 1, 2, or 5 h showed only Ti presence as expected due to the absence of reinforcing particles necessary for the formation of reaction compounds.

XRD data collected on samples with uncoated TiB_2 particles (TB) fired at 1370°C and held for either 0.5, 1, 2, or 5 h showed that TiB formation did occur for every dwell time including the shortest dwell time of 0.5 h. Figure 6 shows the superimposed XRD data collected on samples with uncoated TiB_2 particles and peaks belonging to TiB , TiB_2 , and Ti have been identified. The presence of TiB is indicated by the three low intensity peaks at approximately 29° , 46.5° , and 49° two-theta, a peak around 35° two-theta, that shows up as a shoulder on the high two theta side of a Ti peak, and a doublet at approximately 42° two-theta. The doublet at approximately 42° two-theta matches both position (2θ) and intensity with the lower intensity peak at the lower 2θ position and the higher intensity peak at the higher 2θ position. TiB_2 peaks occur at approximately 27.5° and 44° two-theta. Only the TiB_2 peak at approximately 44° two-theta is present in the data collected on the sample fired for 0.5 h. It is also expected that the peak at approximately 27.5° two-theta would be present as well, however, this is not seen, most likely due to preferred orientation since data were collected on consolidated samples and not powders. The presence of preferred orientation in the data complicates analysis efforts to determine quantitatively the amounts of the various phases present. Neither the XRD data collected on the sample fired for 2 h nor the data collected on the sample fired for 5 h show any evidence of either TiB_2 peak suggesting that by 2 h all the TiB_2 has been reacted and only Ti and TiB phases are present.

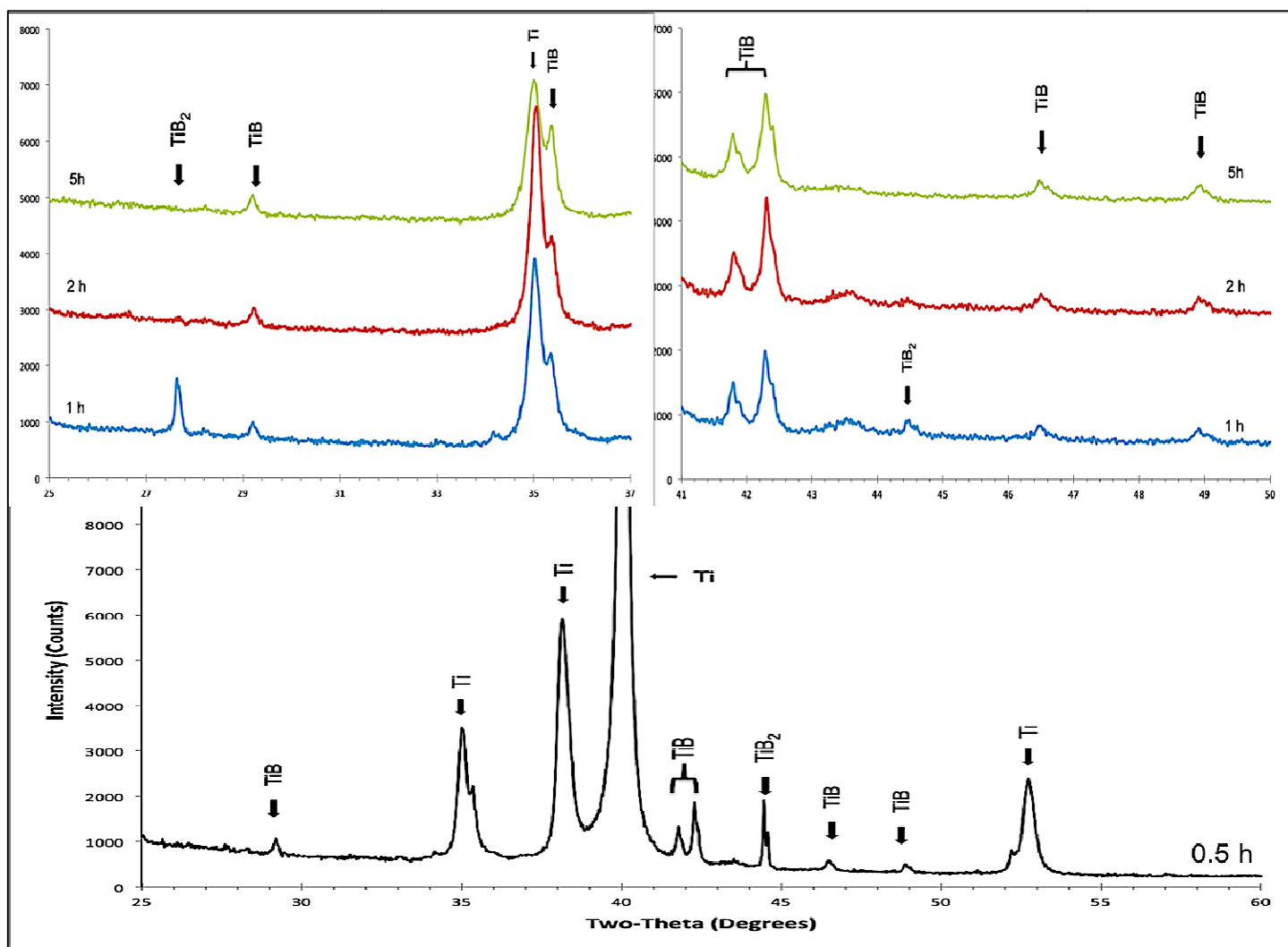


Figure 6. Superimposed XRD data of uncoated samples fired at 1370 °C for 0.5, 1, 2, and 5 h.

Figure 7 shows the superimposed XRD data for samples with the TiB_2 particles coated with N and fired at 1370 °C for 0.5, 1, 2, and 5 h with marked peaks indicating TiB, TiB_2 , and Ti. TiB presence is seen in every sample indicated by the doublet at approximately 42° two-theta, the peak at 35° two-theta and the three smaller peaks at approximately 29°, 46.5°, and 49° two-theta. The presence of the two small peaks at approximately 44° and 27.5° two-theta XRD data suggest a small amount of TiB_2 remains when fired at 1370 °C for up to 2 h, however, at longer hold times TiB_2 is completely consumed and transformed into TiB. The results for the particles coated in N, showing TiB presence, were almost identical to the uncoated TB samples.

Figure 8 shows the superimposed XRD data for samples with the TiB_2 particles coated with C and fired at 1370 °C for 0.5, 1, 2, and 5 h. The presence of TiB is only seen in the XRD data collected on a sample fired 5 h. Additionally, a TiB_2 peak remains visible in all data sets. These results suggest that the carbon coating did in fact exhibit a protective ability. The XRD data also revealed the presence of titanium carbide (TiC), indicated by peaks at approximately 36° and 42° two-theta, resulting from the reaction of the Ti matrix with the carbon coating.

By comparing the XRD data collected on all samples fired at 1370 °C for 1 h, as shown in Figure 9, some useful observations can be made. The TiC peaks are only present in the carbon coated C sample. Further comparison reveals the difference between the peaks at approximately 42° two-theta. The doublet at approximately 41.5° and 42.5° two-theta in data collected on samples of both the N coated TiB_2 particles and the uncoated TiB_2 particles (TB) samples indicate TiB formation as observed previously. A larger single peak exists at approximately 42° two-theta in data collected on the sample with C coated particles indicating TiC formation and not attributed to TiB formation.

Overall, XRD data revealed that TiB did form according to Equation 1 in all samples with uncoated TiB_2 particles (TB). The nitrogen coating was unsuccessful in preventing TiB formation and the XRD data was similar to that collected on samples with uncoated particles (TB). This was most likely due to unsuccessful nitrogenization and formation of a BN coating. Due to this result the N coated samples were eliminated from additional testing. The carbon coating proved successful in preventing TiB formation at dwell times up to 2 h. TiB formation was only present in sample (C5) that was held at temperature for 5 h. TiC formation occurred in the samples with C coated TiB_2 particles resulting from a reaction between the Ti matrix and the carbon coating.

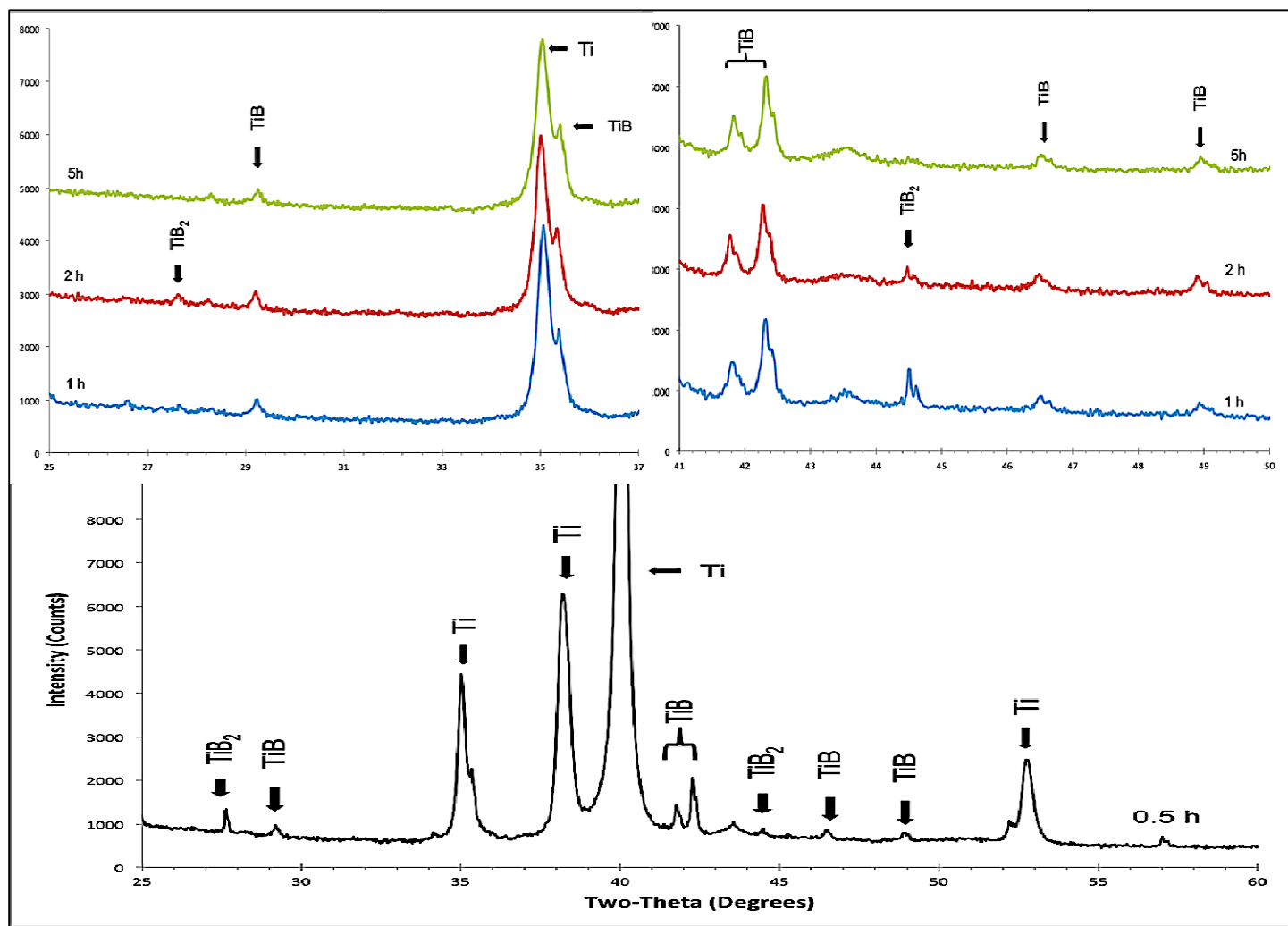


Figure 7. Superimposed XRD data of N coated samples fired at 1370 °C for 0.5, 1, 2, and 5 h.

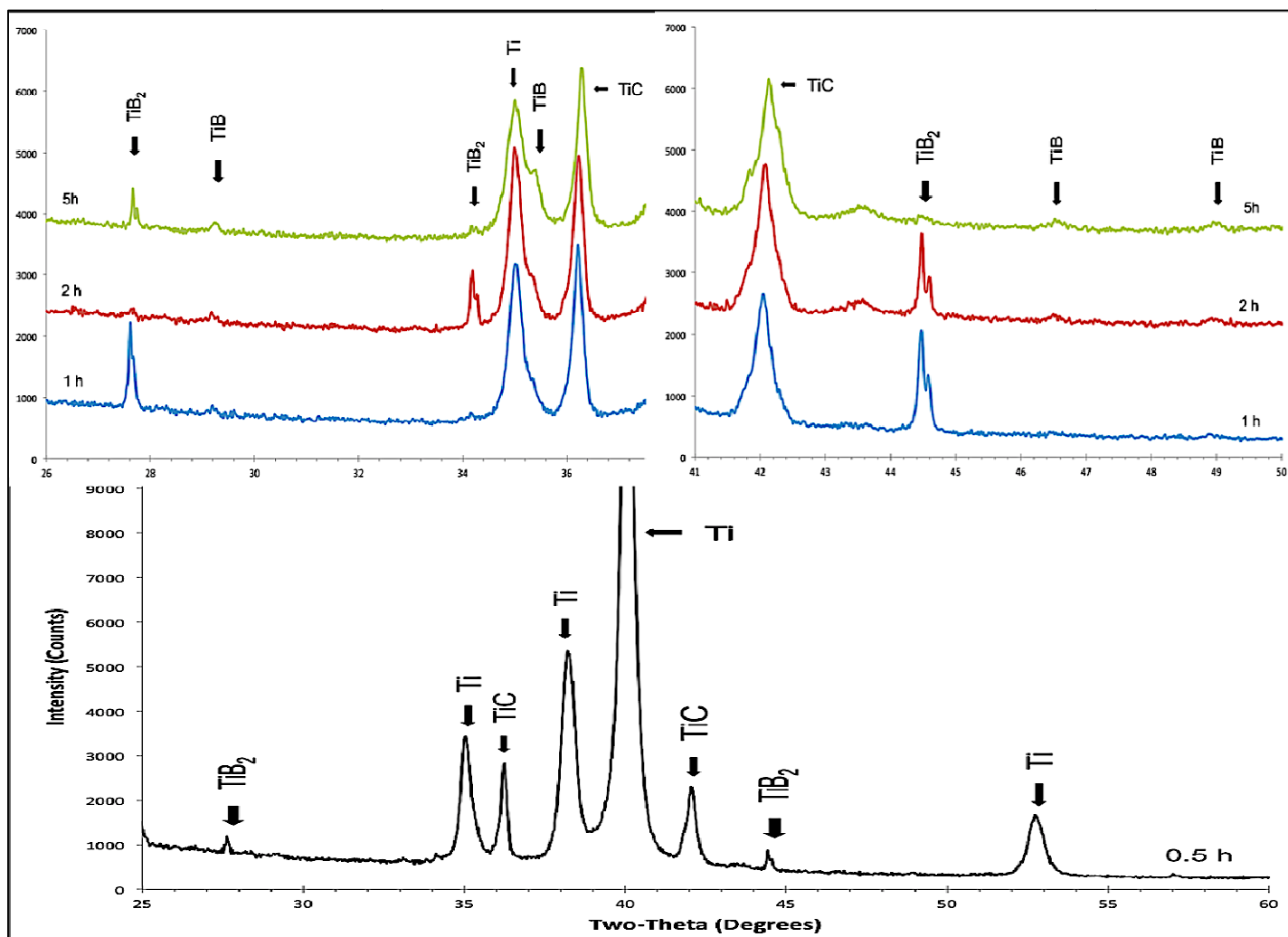


Figure 8. Superimposed XRD data of C coated samples fired at 1370 °C for 0.5, 1, 2, and 5 h.

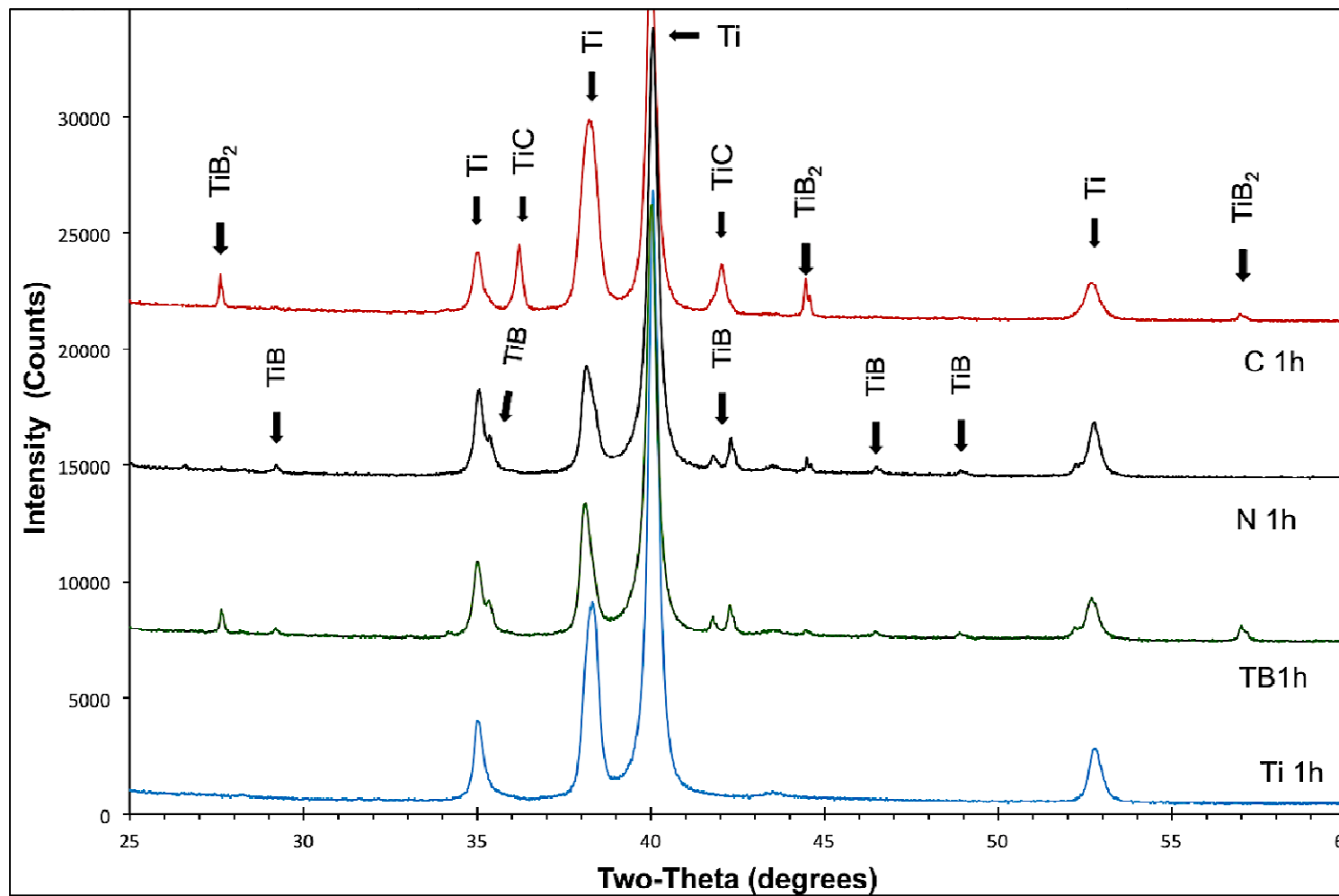


Figure 9. Superimposed XRD data comparing samples with uncoated, N coated, and C coated TiB_2 particles with a sample of commercially pure Ti. All samples were fired at 1370 °C for 1 h.

Light Microscopy Characterization

Lower resolution light microscopy enabled visual observations of the particles, coatings, and reaction products supporting the results based on analyzing the XRD data and supported that TiB formation did occur for all dwell times for samples with uncoated TiB₂ particles (TB). Figures 10, 11, and 12 depict the samples with uncoated TiB₂ particles and held at 1370 °C for 1, 2 and 5 h, respectively.

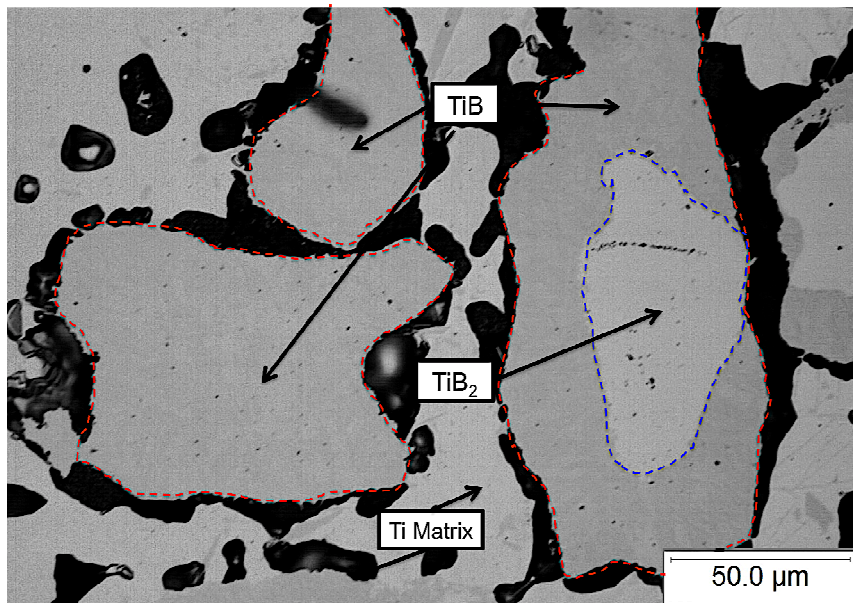


Figure 10. Uncoated TiB₂ particles (TB1) held at 1370 °C for 1 h (400X) showing the TiB reaction layer growing inward.

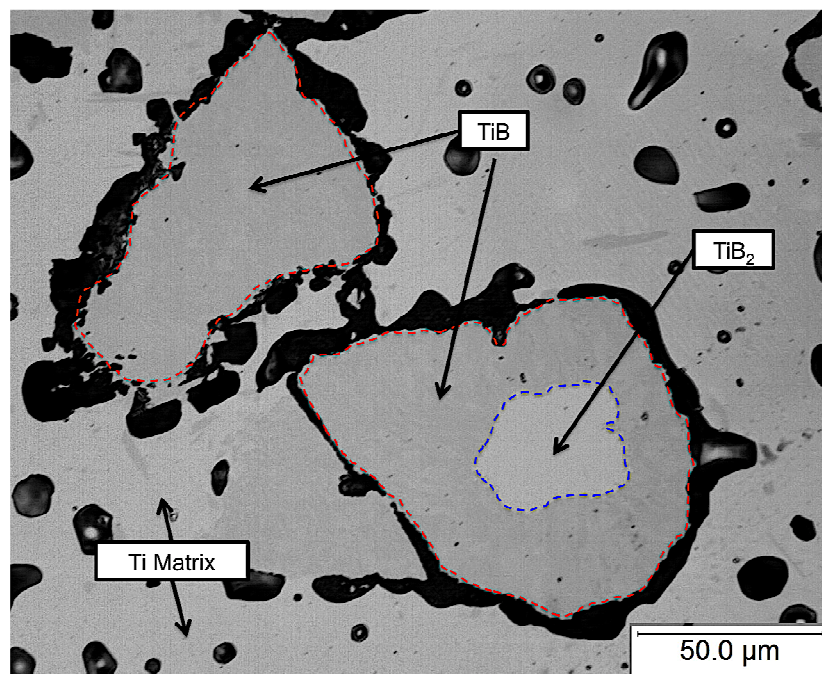


Figure 11. Uncoated TiB_2 particles (TB2) held at 1370°C for 2 h (400X).

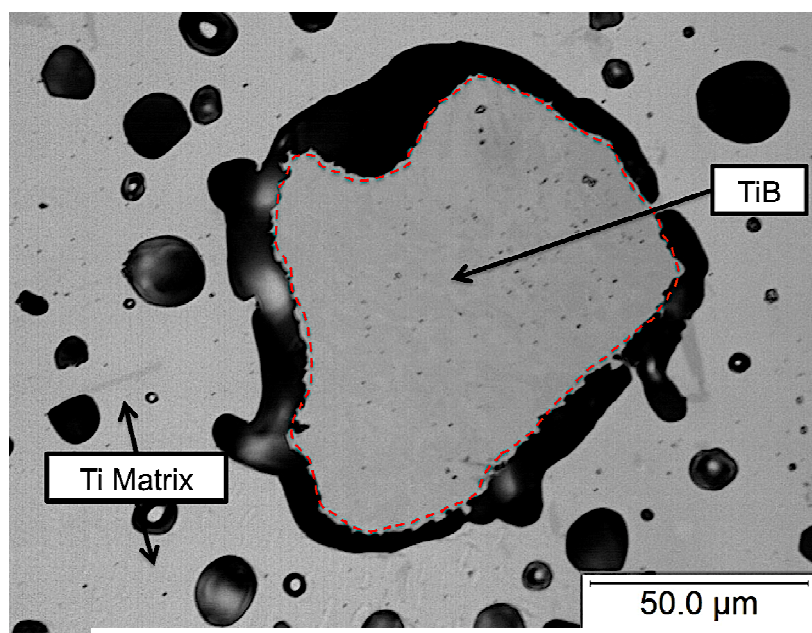


Figure 12. Uncoated TiB_2 particles (TB5) held at 1370°C for 5 h (400X). Complete conversion of the TiB_2 particle into TiB is shown.

The TiB_2 particle and TiB reaction layer can be discerned by the contrasting shades and show a TiB formation layer is present and growing inwards from the interface between the particle and the matrix. In Figure 10, three particles can be seen, two of which have already been completely transformed into TiB while the larger particle shows a small amount of remaining TiB_2 at the core. Figure 11 is similar to Figure 10, however, with a smaller amount of remnant TiB_2 at the core. Figure 12 shows that when held at 1370 °C for 5 h, the TiB_2 particles are completely consumed by the matrix and transformed into TiB. These observations agree with the XRD data suggesting that TiB formation does occur in the samples with uncoated TiB_2 (TB) particles. Microscopy data collected on samples with N coated particles (N) were almost identical in appearance to samples with the uncoated TiB_2 particles supporting that formation of a BN coating was unsuccessful and hence TiB formation was not prevented. TiB formation was seen to be present and growing inward even at the shortest dwell time of 0.5 h.

Figures 13, 14, and 15 were collected on samples with C coated TiB_2 particles (C) and held at 1370 °C for various dwell times of 1, 2, and 5 h respectively.

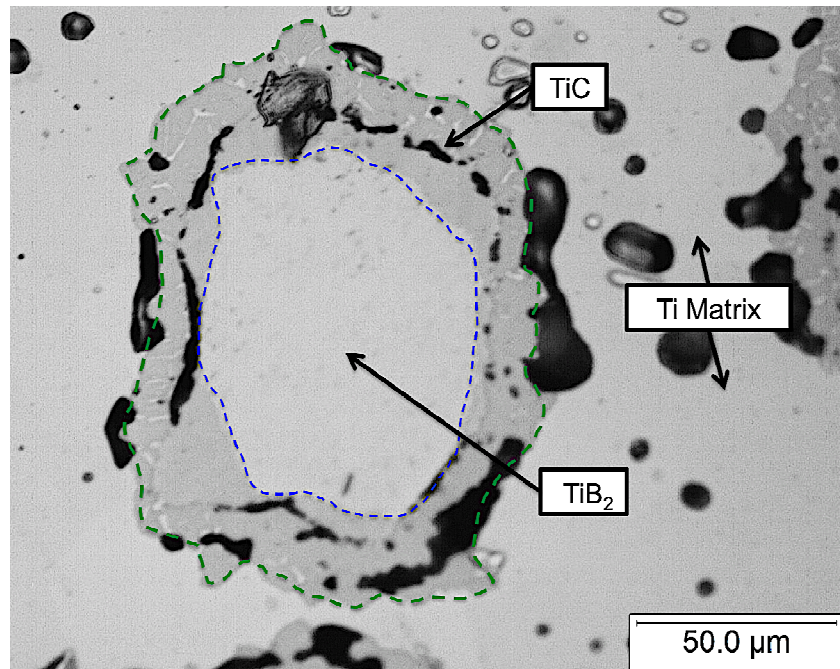


Figure 13. Carbon coated TiB_2 particles (C1) held at 1370 °C for 1 h (400X).

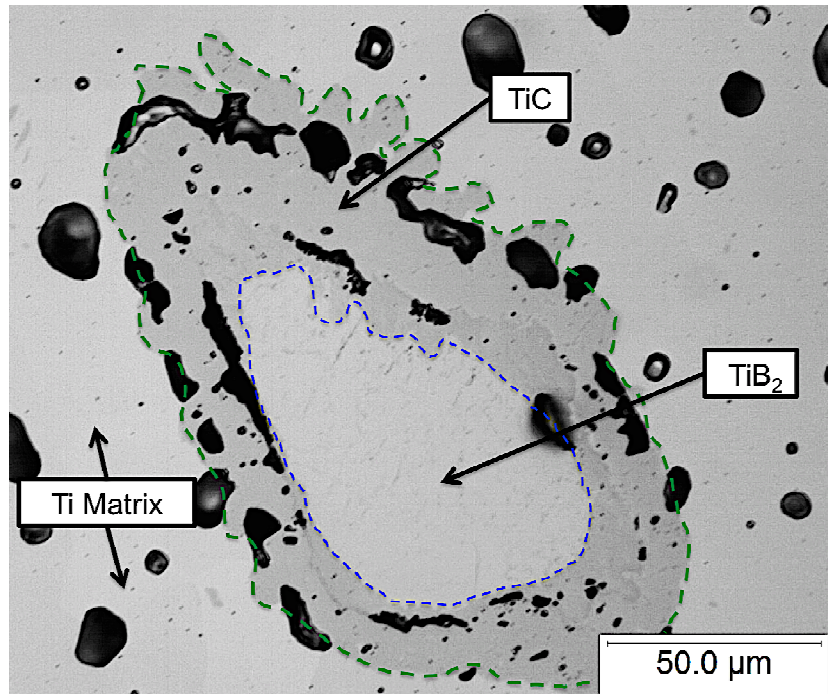


Figure 14. Carbon coated TiB_2 particles (C2) held at 1370 °C for 2 h (400X).

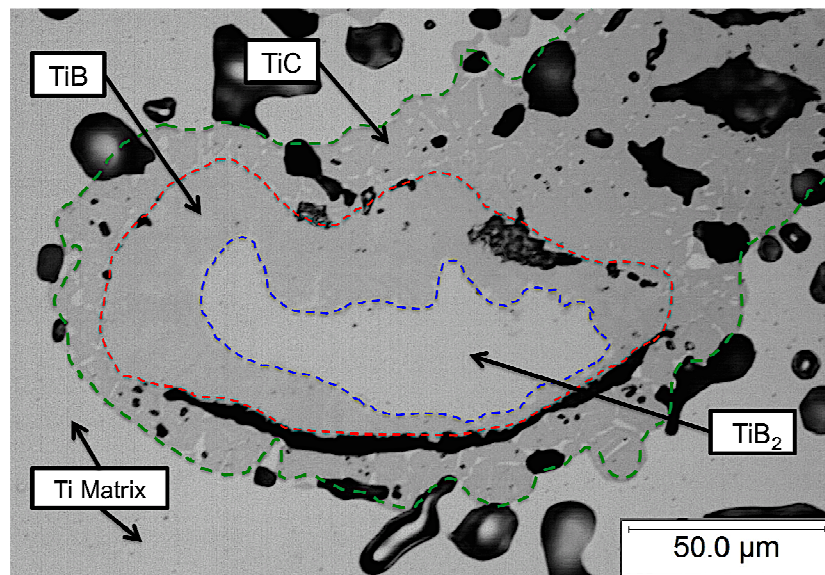


Figure 15. Carbon coated TiB_2 particles (C5) held at 1370 °C for 5 h (400X). The coating breakdown with TiB formation proceeding inward is shown.

These figures show that for a dwell time of 1 h the coating is present and extends out slightly into the matrix while the majority of the TiB_2 particle remains unreacted and for a dwell time of 2 h the protective coating is still intact with the TiB_2 remaining unreacted. However, for a dwell time of 5 h the coating has failed indicated by the inward growth of presumed TiB as it consumes the TiB_2 particle.

Additional general observations concluded from the images shown in Figures 10–15 include that the TiB_2 particles have a range of shapes, some particles are more spheroidal in shape while some are have more non-symmetrical shapes with sharp edges. Particles in Figures 14 and 15 are larger than 50 microns indicating that the sieving process was successful. All figures also indicate that the material is porous with numerous voids and pores.

These results show that XRD characterization is an important analysis technique providing the ability to identify TiB, TiC, and TiB_2 while microscopy allowed the coatings behavior to be visually observed and imaged. Coupled together, these two techniques provide a thorough understanding of the in situ conversion of TiB_2 showing that the carbon coating was successful in preventing observable TiB_2 conversion for samples fired at 1370 °C with dwell times up to 2 h. At 1370 °C a dwell time of 5 h is excessive but allows for investigating the coating durability and to better understand how long the coating integrity could potentially remain intact. Another beneficial observation was that the carbon coating reacts with the Ti matrix to form TiC. This in situ reaction is desired since TiC exhibits superior ballistic properties such as a high hardness and Young's modulus over pyrolytic carbon. The samples with N coated TiB_2 particles proved unsuccessful and was most likely due to unsuccessful coating formation on the TiB_2 particles. Characterization of the samples with uncoated TiB_2 particles (TB) indicated that the conversion of TiB_2 into TiB does occur during processing, even at the short hold time of 0.5 h and that increasing the dwell time increases TiB formation until complete conversion is reached at 5 h. This TiB_2 conversion into TiB is the primary problem that this study aimed to overcome in order to produce an improved armor material.

Constant Time/Variable Temperature

Based on the results of the variable time/constant temperature experiments a series of experiments where the samples were held for 0.5 h and fired at either 900, 1000, 1100, 1200, or 1300 °C were undertaken on samples containing uncoated TiB_2 particles, for comparison to samples with C coated TiB_2 particles.

XRD Characterization

XRD data were collected to identify compounds present in each sample mainly focusing on TiB, TiB_2 , and TiC. The shortest hold time of 0.5 h was chosen to determine the effect of temperature on the consumption of TiB_2 and

the formation of TiC. As a reminder, MoK α radiation was used to collect XRD data (as compared to CuK α for the variable time/constant temperature experiments) on these samples resulting in the peaks positions being shifted when comparing to the data collected on samples fired at variable times and constant temperature. Figure 16 shows the superimposed XRD data of the samples with uncoated TiB₂ particles and reveals that the conversion of TiB₂ into TiB did occur but not significantly until a temperature of 1100 °C, however, significant consumption of TiB₂ was observed at the highest temperature of 1300 °C.

The presence of TiB₂ can be determined from a main peak just above 20° two-theta and three smaller peaks at 12.5, 15.5, and 25.5° two-theta compared to TiB formation that can be identified by the doublet at approximately 19° two-theta along with four smaller peaks at 13.5, 21, 22, and 23.5° two-theta. Data collected at the lower temperature of 900 (TB6), 1000 (TB7), and 1100 °C (TB8), show that TiB₂ is intact with little to no formation of TiB. However, at 1200 °C (TB9) significant TiB formation can be identified as the doublet appears at approximately 19° two-theta and the four smaller TiB peaks begin to appear. At 1300 °C (TB10) TiB formation increases as indicated by the increase in intensity of the doublet at 19° two-theta and the additional four smaller peaks. By comparing the data collected at all temperatures the concentration of TiB₂ is seen to continually decrease with increasing temperature indicated by the decrease in the intensity profile of all four TiB₂ peaks. However, a very small portion of TiB₂ is still present at 1300 °C. Correspondingly, the intensity of the TiB peaks increase indicating that the conversion of TiB₂ into TiB is occurring.

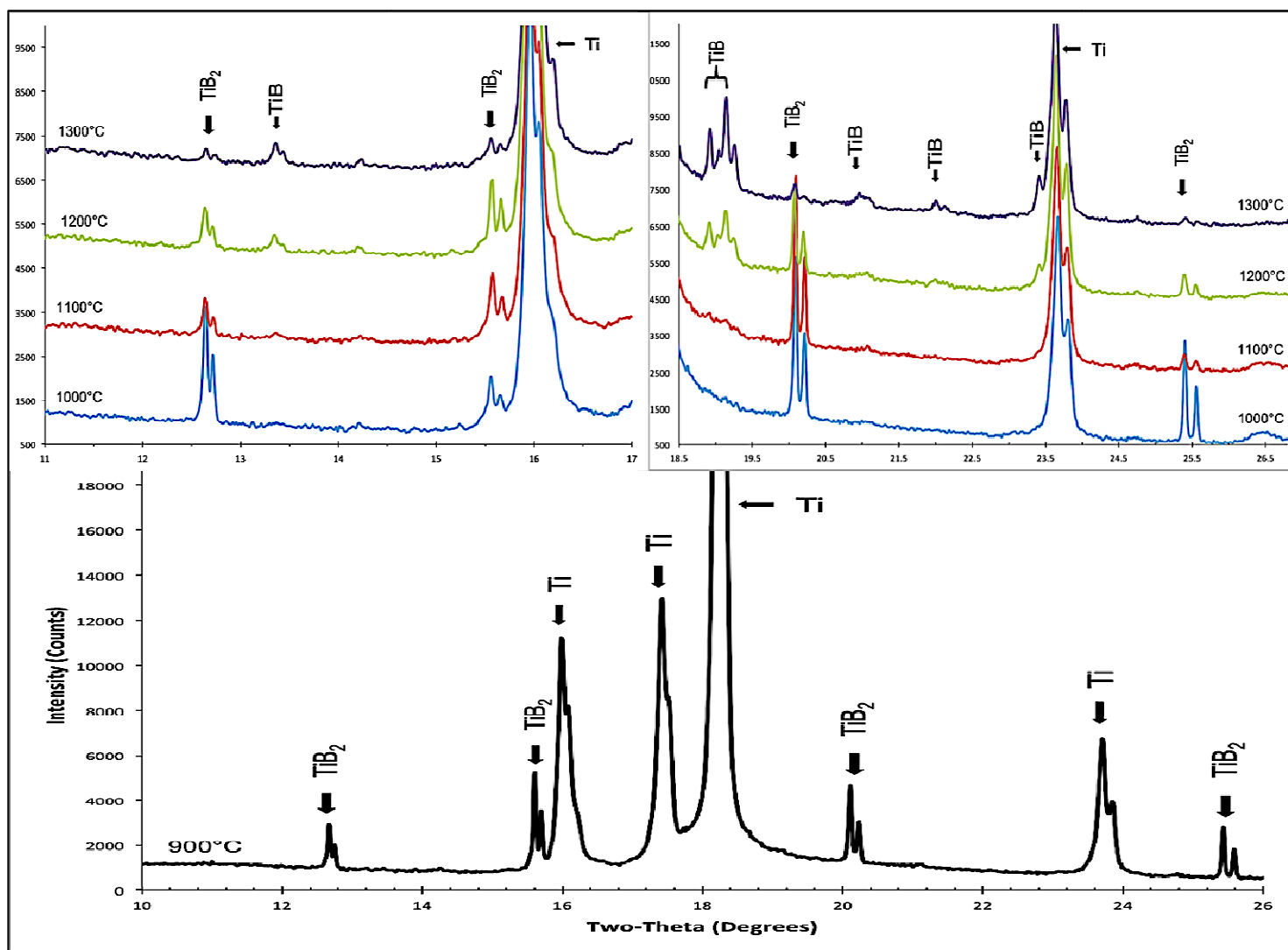


Figure 16. Superimposed XRD data for samples with uncoated TiB_2 particles and fired for 0.5 h at 900, 1000, 1100, 1200, and 1300 °C.

The data collected on samples with C coated TiB_2 particles revealed that the carbon coating was successful at all temperatures in protecting the TiB_2 particles from reaction with the Ti matrix. Figure 17 shows the superimposed XRD data for the samples with C coated TiB_2 particles fired for 0.5 h at 900, 1000, 1100, 1200, or 1300 °C and shows that TiB_2 consumption is not seen throughout the temperature range. The main TiB_2 peak, just above 20° two-theta, is present at all temperatures and the three smaller peaks at 12.5, 15.5, and 25.5° two-theta also did not show any trend of decreasing intensity indicative of a decrease in TiB_2 concentration. The characteristic TiB peaks at 13.5, 21, 22, and 23.5 two-theta along with the doublet at 19° two-theta are not present in any of the data collected on samples with C coated TiB_2 particles. However, TiC presence is indicated by peaks at 16.5 and 19° two-theta.

By comparing Figures 16 and 17, the TiC and TiB peaks can be differentiated by their shape and intensities. The XRD data show that the presence of TiC formation did not occur until 1000 °C (C7). The two TiC peaks appear weak in intensity for the data collected on the sample fired at 1000 °C (C7) but increased in intensity with increasing temperature for the samples fired at 1100 and 1200 °C. At 1200 °C (C9) the TiC concentration has reached its maximum as indicated by the intensity of the TiC peaks remaining constant for both the data collected on the 1200 and 1300 °C data. After 900 °C the carbon coating begins to transform into TiC from reaction with the Ti matrix. A couple important results can be revealed by examining the XRD data including that both the samples with uncoated and C coated TiB_2 particles show significant TiB_2 presence up to a temperature of 1100 °C. However, at higher temperatures the TiB_2 peak intensities begin to decrease in the samples with uncoated TiB_2 particles compared to the samples with C coated TiB_2 particles where the peak intensities remain constant. The TiB only appears in the data collected on samples where the TiB_2 particles are uncoated and not at all in the data collected on samples where the TiB_2 particles are C coated. Conversely, the TiC peaks are only seen in the data where the TiB_2 particles are C coated and not in the data where the TiB_2 particles are uncoated. These results show that TiB begins to form in the samples with uncoated TiB_2 particles leading to depletion of TiB_2 whereas TiB_2 conversion is eliminated in the samples with TiB_2 C coated particles due to the protective coating.

Overall, the XRD data reveal some notable results. First, TiB formation was confirmed in the samples with uncoated TiB_2 particles fired at 1200 and 1300 °C and TiB formation leads to the depletion of TiB_2 following Equation 1. Second, the carbon coating of TiB_2 particles proved successful in preventing the conversion of TiB_2 into TiB. Finally, the carbon coating reacted with the matrix to produce TiC and reached a presumed maximum conversion at 1200 °C.

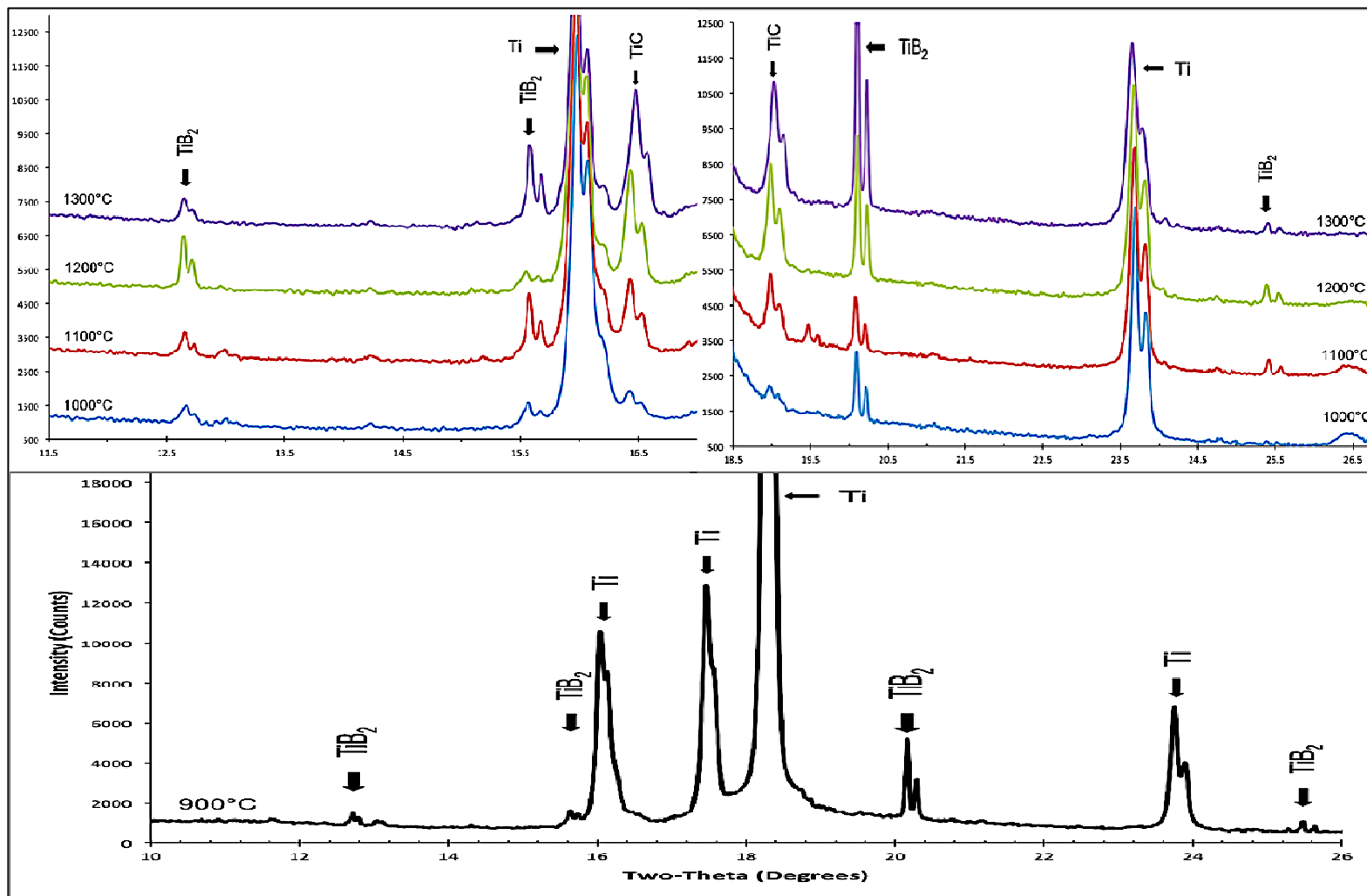


Figure 17. Superimposed XRD data on samples with C coated TiB_2 particles fired for 0.5 h at 900, 1000, 1100, 1200, and 1300 °C.

SEM Characterization

High resolution SEM analysis enabled detailed visual observations of the particles, coatings, and reaction products and corroborated the findings of the previous XRD analysis. TiB_2 depletion was observed in samples with uncoated TiB_2 particles along with TiC formation and TiB_2 preservation in the samples with C coated TiB_2 particles. Figures 18-20 show the growth of TiB with increasing temperature for samples fired for 0.5 hour at 900, 1100, and 1300 °C.

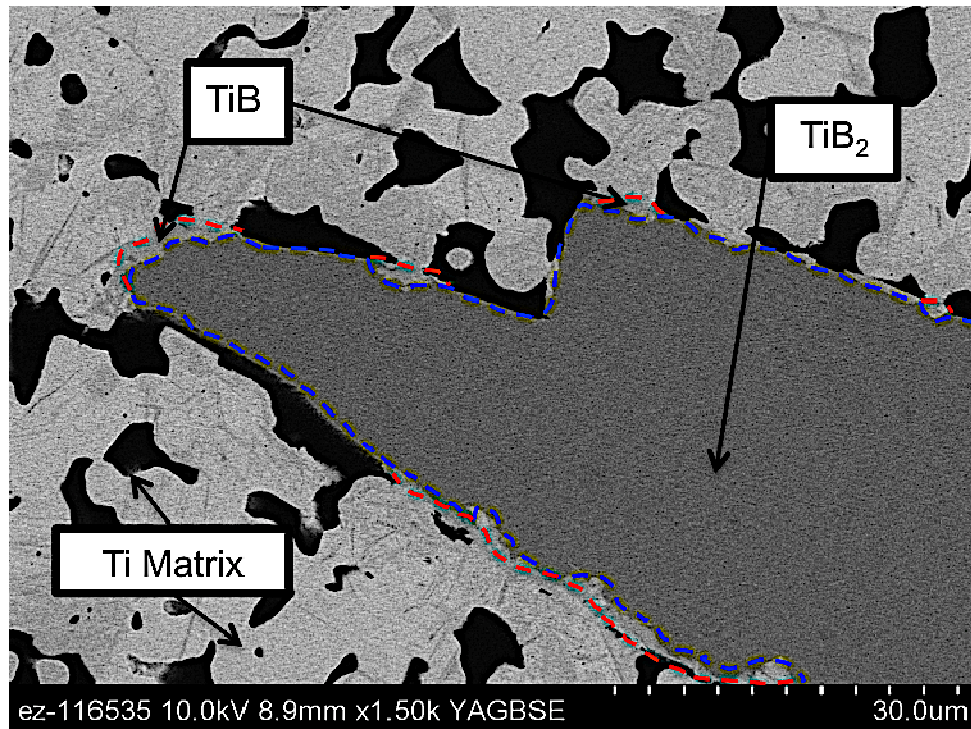


Figure 18. SEM image of an uncoated TiB_2 particle fired for 0.5 at 900 °C (1500X).

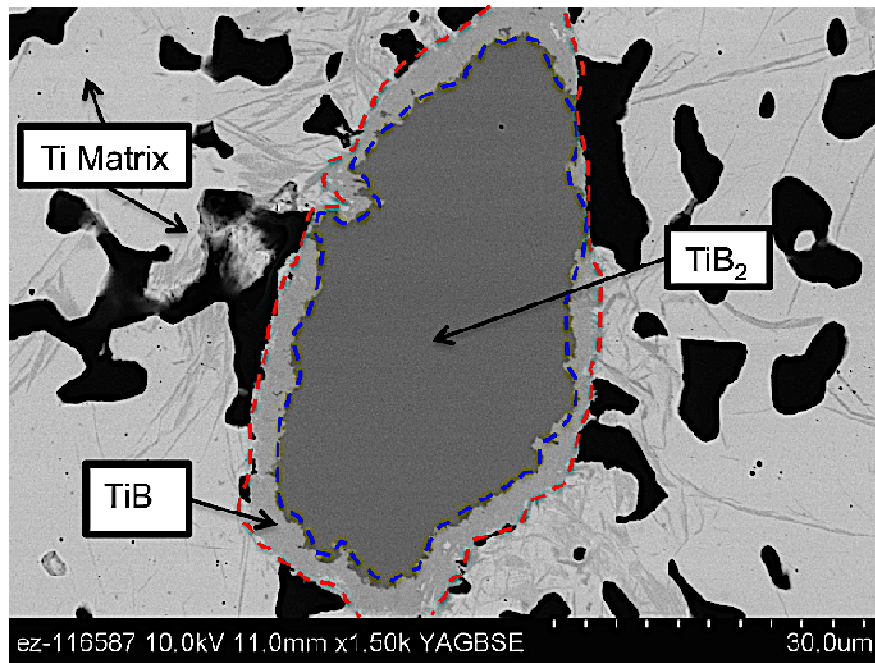


Figure 19. SEM image of an uncoated TiB₂ particle fired for 0.5 h at 1100 °C (1500X).

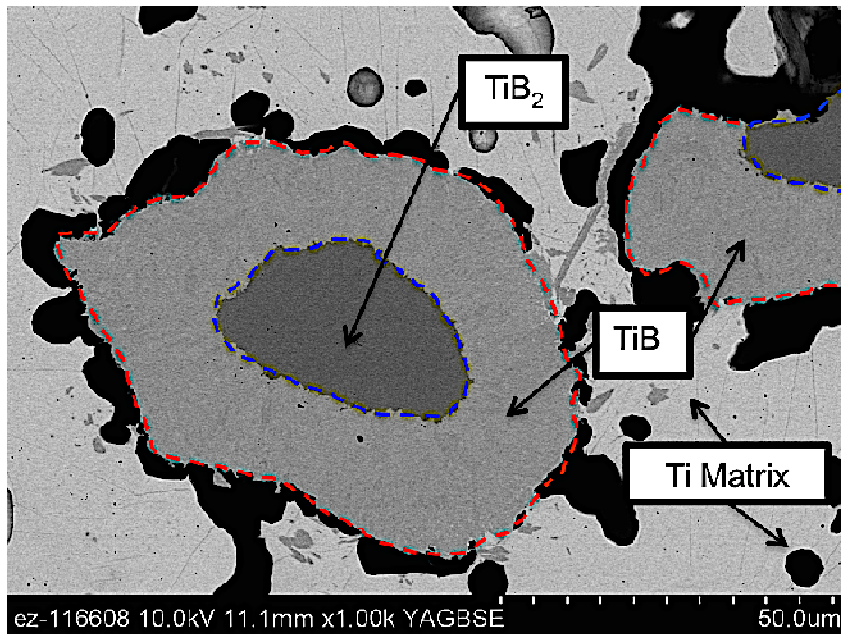


Figure 20. SEM image of an uncoated TiB₂ particle fired for 0.5 h at 1300 °C (1000X).

Figure 18 shows a nonsymmetrical uncoated TiB_2 particle fired for 0.5 h at 900 °C. Although the previous XRD data showed no observable TiB formation (most likely it is under the detection limit), the image reveals that a minor amount of TiB had formed at this temperature as indicated by the lighter shaded TiB, seen forming at the interface of the particle at the interface with the matrix. The material is porous (black indicates pores and voids) and not all of the exterior surface of the TiB_2 particle was in contact with the matrix. TiB formation only occurred where there was direct contact between the particle and the matrix.

Figure 19 shows a more symmetrical uncoated particle fired at 0.5 h at 1100 °C (TB8). TiB is seen growing inward and consuming the TiB_2 particle by forming a complete shell on the outer section of the particle. TiB formation is also seen by the appearance of fine TiB whiskers growing outward from the interface.

Figure 20 shows a spheroidal particle fired for 0.5 h at 1300 °C (TB10), the highest temperature investigated. TiB growth has proceeded inward, transforming a major part of the TiB_2 particle into TiB. A small amount of TiB_2 does remain intact but only at the core of the particle. TiB whiskers or needles are also seen extending out into the matrix. By comparing the three uncoated particle images, the inward growth of TiB leading to consumption of the TiB_2 particles can be seen.

Figures 21-23 below show SEM images collected on samples with C coated TiB_2 particles fired for 0.5 h at 900, 1100, and 1300 °C, respectively. Figure 21 shows a C coated spheroidal TiB_2 particle in the Ti matrix and fired for 0.5 h at 900 °C. Coating of the particles was proven successful by the visible black C coating encasing the particle that was determined to be 5-10 μm thick along with no observable TiB or TiC formation. The TiB_2 particle and carbon coating both remain intact and unreactive with the matrix.

At a higher firing temperature of 1100 °C, shown in Figure 22, the C coating is partially transformed to TiC, due to both the C coating and TiC existing at this temperature, and TiC is shown to grow inward from the interface between the C coating and the Ti matrix. The TiB_2 particle continues to remain intact and protected from the matrix as indicated by no TiB presence.

Figure 23 depicts a C coated TiB_2 particle fired for 0.5 at 1300 °C. The protective coating remains successful in preventing the conversion of TiB_2 into TiB. At this temperature however, the carbon coating has almost been completely converted into TiC and little to none of the original carbon coating remains. The TiC shell has formed around the particle; however, it does not protrude into the particle, as is the case with the samples from with the uncoated TiB_2 particles.

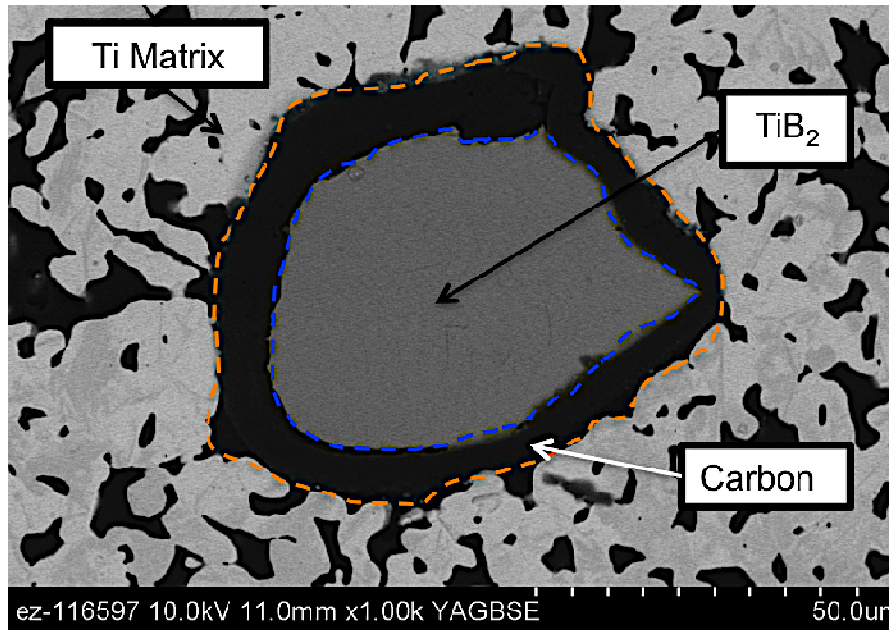


Figure 21. SEM image of a C coated TiB₂ particle fired for 0.5 h at 900 °C (1000X).

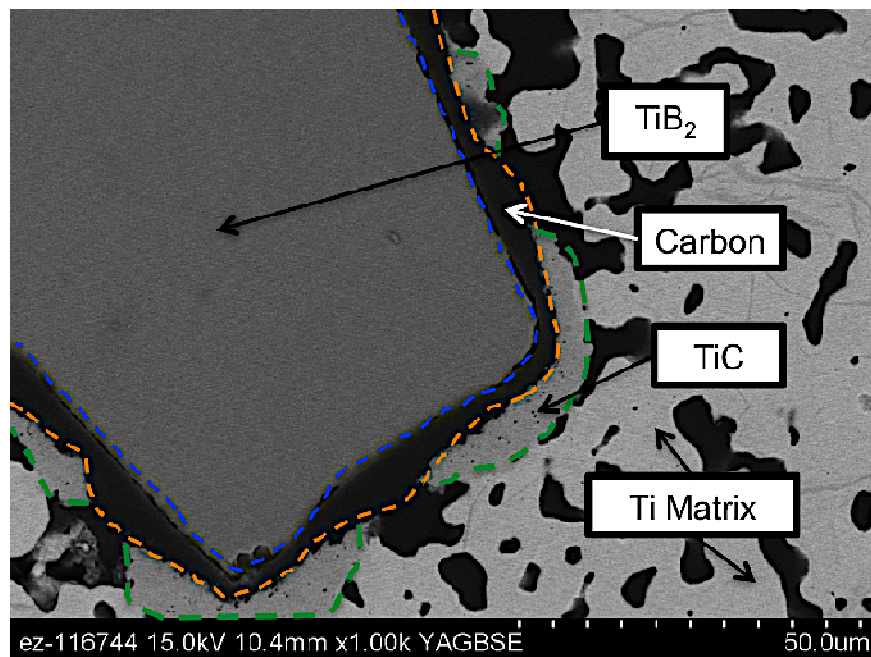


Figure 22. SEM image of a C coated TiB₂ particle fired for 0.5 h at 1100 °C (1000X).

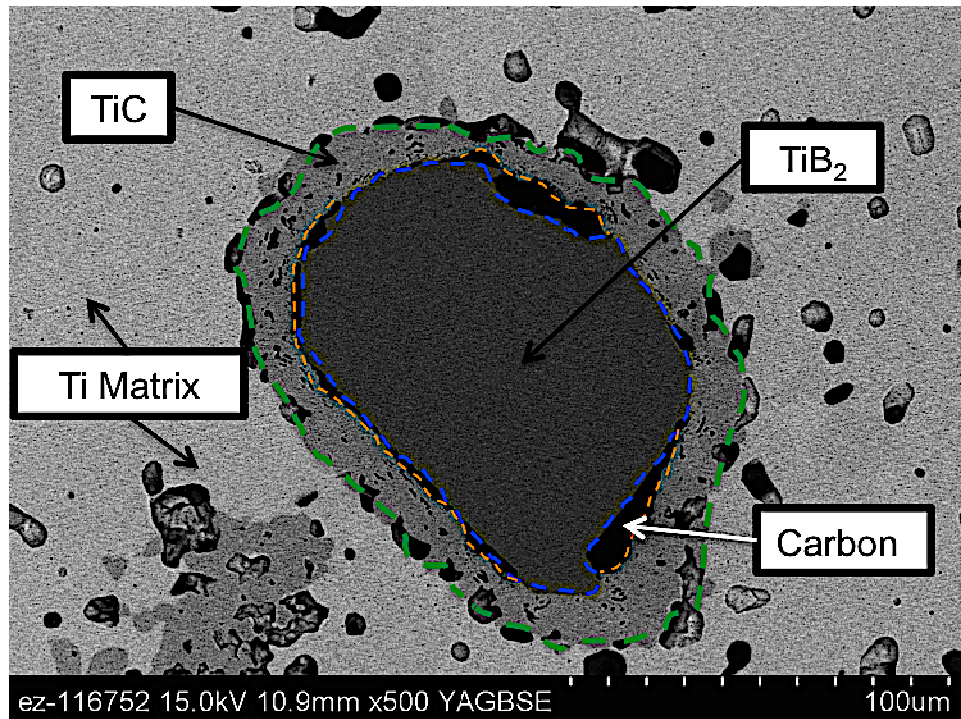


Figure 23. SEM image of a C coated TiB_2 particle fired for 0.5 h at 1300 °C (500X).

The SEM analysis corroborates the findings of the XRD characterization. As predicted, TiB_2 conversion into TiB did occur in all uncoated TiB_2 samples and the conversion increased with increasing temperature indicated by the TiB inward growth into the TiB_2 particle. At the lowest temperature of 900 °C, minimal TiB formation was seen, however, at the highest temperature of 1300 °C, a large portion of the particle was converted into TiB . The C coating proved successful in protecting the TiB_2 particles from reaction with the Ti matrix at all temperatures evaluated and was observed to be fairly uniform with a thickness of 5-10 μm . The coating remained C at the lowest temperature, however, with increasing temperature, the C coating started to react with the matrix forming TiC . At the highest temperature of 1300 °C, nearly all the C coating was converted into TiC forming a protective shell.

Hot Pressing

Results from the variable time/constant temperature and constant time/variable temperature experiments were used to determine the parameters for experiments focused on the protective ability of the C coating using the hot pressing technique. Since full reaction between the C coating and the Ti matrix is desirable in order to fully convert the coating into TiC and provide a strong interface between the particle and the matrix a hot pressing temperature of 1200 °C was chosen. Samples were characterized using XRD and microscopy. Additionally, since the mechanical integrity is important to the applications of these materials, impact tests were conducted to determine the relative impact strengths between the three materials. Hot pressing will be the best processing route to achieve a fully dense high performance composite plate.

XRD Characterization

As in the previous studies XRD characterization was performed to identify the presence of TiB, TiB₂, and TiC. The results revealed that TiB did occur in the uncoated TiB₂ particles whereas the C coating successfully prevented the conversion of TiB₂ into TiB. Figure 24 compares the XRD data for the pure Ti, Ti matrix with uncoated TiB₂ particles, and Ti matrix with C coated TiB₂ particles. A strong intensity TiB₂ peak at 44° two-theta is present in the data collected on the sample with C coated TiB₂ particles while the XRD data shows a peak with diminished intensity for the sample with uncoated TiB₂ particles. TiC presence is also indicated by two peaks at 42 and 36° two-theta in the sample with C coated TiB₂ particles.

Table 8 contains the crystal structure information including the space groups and unit cell parameters used to calculate a rough approximation of the wt% of identified phases. TiB formation did occur in the samples with uncoated TiB₂ particles resulting in roughly 6 wt% TiB. The C coating proved successful in preventing TiB formation and no TiB was identified in the sample with the C coating. However, the C coating did react with the matrix to form TiC. The absence of TiB signifies that the TiB₂ content was conserved.

From the XRD characterization of the hot pressed samples it was shown the Ti matrix does react with the TiB₂ particles to form TiB in the samples with uncoated TiB₂ particles. The C coating again proved to effectively protect the TiB₂ particles during hot pressing from being converted into TiB. This was indicated by the absence of TiB peaks and presence of TiB₂ peaks in the XRD data. Also, XRD data show that TiC was formed from the reaction of the carbon coating and the Ti matrix in the sample with C coated TiB₂ particles.

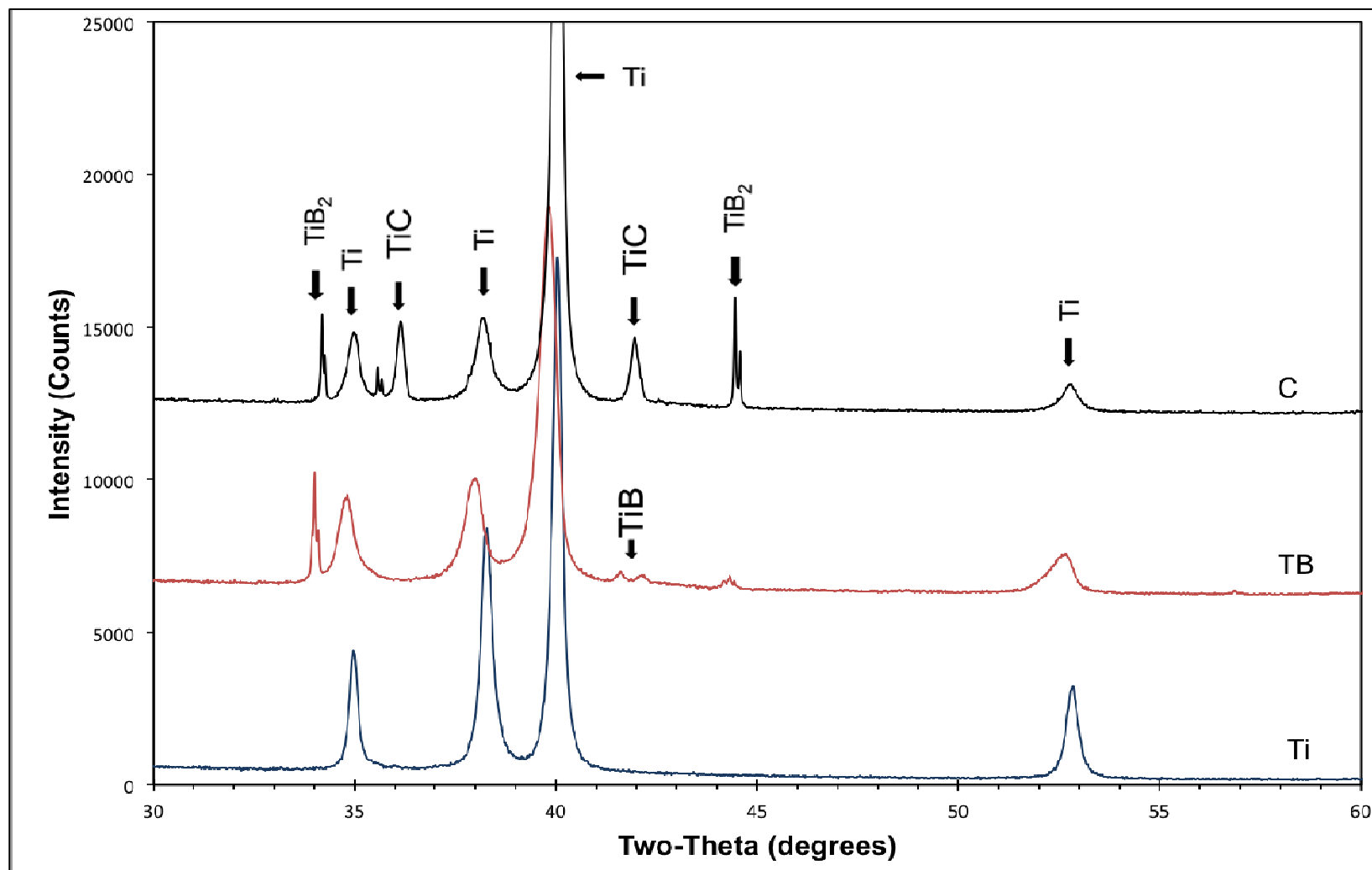


Figure 24. Superimposed XRD data for the hot pressed samples C coated TiB_2 particles, uncoated TiB_2 particles, and a sample without particles.

Table 8. Crystal system, space group, and lattice parameters along with approximate wt% for compounds in hot pressed samples.

Sample	Compound	wt %	Crystal System Space Group	a (Å)	b (Å)	c (Å)
				α (°)	β (°)	γ (°)
T CP-Ti	Titanium	100	Hexagonal	2.961	2.961	4.701
			$P6_3/mmc$ (194)	90	90	120
TB Uncoated Ti + TiB₂	Titanium	87	Hexagonal	2.971	2.971	4.732
			$P6_3/mmc$ (194)	90	90	120
	TiB ₂	6	Hexagonal	3.040	3.040	3.241
			$P6/mmm$ (191)	90	90	120
	TiB	7	Orthorhombic	6.119	3.069	4.576
			$Pnma$ (62)	90	90	90
C Coated Ti + TiB₂	Titanium	80	Hexagonal	2.961	2.961	4.710
			$P6_3/mmc$ (194)	90	90	120
	TiB ₂	6	Hexagonal	3.028	3.028	3.232
			$P6/mmm$ (191)	90	90	120
	TiC	14	Cubic	4.305	4.305	4.305
			$Fm\bar{3}m$ (225)	90	90	90

Microscopy

Optical microscopy was used to view the appearance of the coating and particles after hot pressing. The images showed similar results to the studies performed at constant time/variable temperatures and variable times/constant temperature. Figure 25 is a micrograph showing an uncoated TiB_2 particle showing TiB growing inward from the interface and depleting the TiB_2 . Figure 26 shows a C coated TiB_2 particle, here the TiB_2 remains unreacted with no appearance of TiB growth and a TiC outer shell is seen to have formed from the reaction between the C coating and the Ti matrix. The C coating has not completely converted into TiC as indicated by the appearance of some remaining carbon.

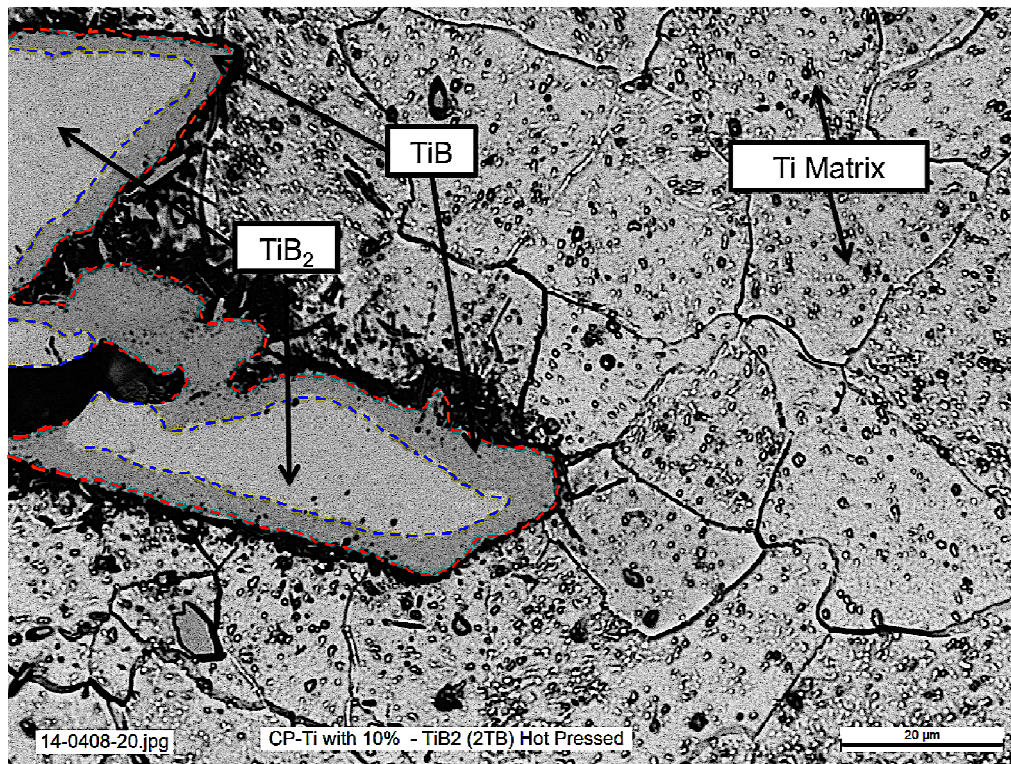


Figure 25. Image of an uncoated TiB_2 particle in a hot pressed sample.

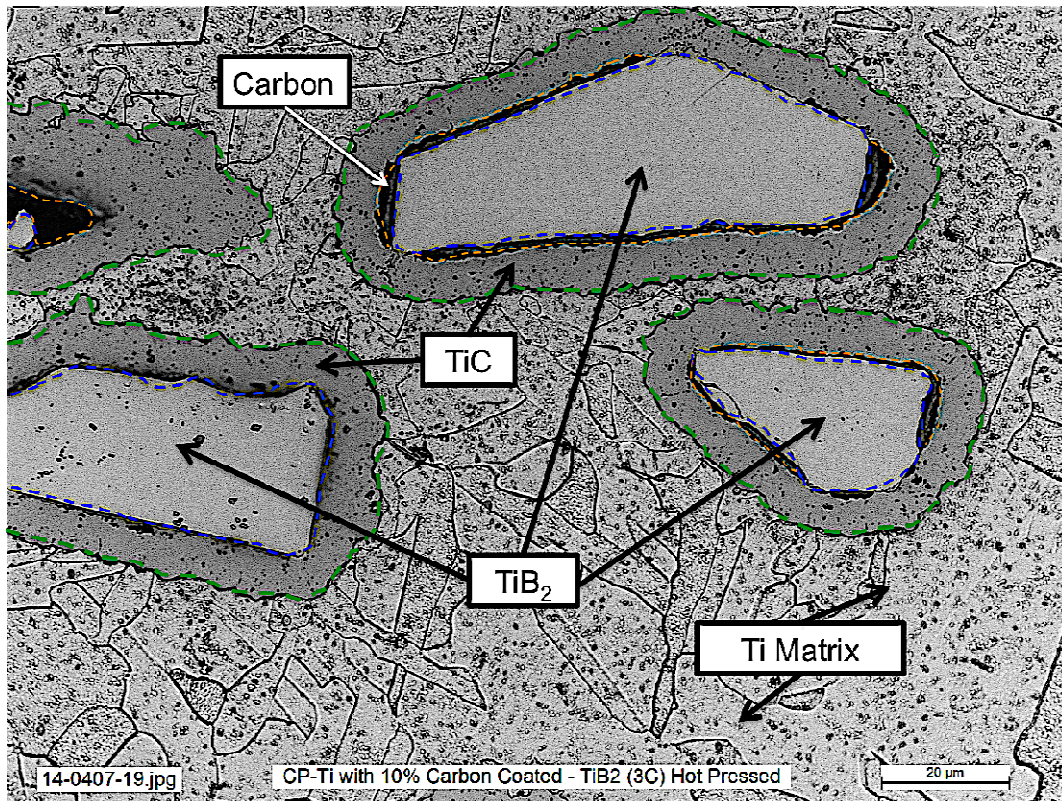


Figure 26. Image of C coated TiB₂ particles in a hot pressed sample.

Charpy Impact Testing Results

Mechanical characterization using charpy impact tests was conducted to determine how the impact strength of the material was affected by addition of the C coating along with a comparison between unreinforced Ti and TiB₂ particle reinforced materials. All materials showed low impact values with only small differences. The hot pressed unreinforced Ti bars exhibited the largest impact energies, followed by the bars with C coated TiB₂ particles, and then the bars with uncoated TiB₂ particles. The bars with uncoated TiB₂ particles had such low impact energies that they were imperceptible by the testing device resulting in values of 0. Table 9 shows the five test samples cut from each material and their corresponding impact energies. Ti alone is more ductile with a lower Young's modulus and has higher impact strength accounting for its improved properties as determined by the impact test. Although impact testing does not directly correlate to ballistic performance, the higher impact strength, even though by just a minute amount, of the bars fabricated from C coated TiB₂ particles over the bars fabricated with uncoated TiB₂ particles shows promise that the composite with C coated TiB₂ particles could lead to an improved armor system.

Table 9. Charpy impact test results.

Material	Sample Number	Dial Energy ft-lbs
Unreinforced Ti	1	1
	2	0.9
	3	1
	4	0.9
	5	1
Uncoated TiB ₂ particles in a Ti matrix	1	0
	2	0
	3	0
	4	0
	5	0
C coated TiB ₂ particles in a Ti matrix	1	0.15
	2	0.2
	3	0.1
	4	0.1
	5	0.05

CHAPTER 4

CONCLUSIONS

This study presents an innovative scheme to produce a Ti/TiB₂ composite in which the TiB₂ reinforcing particulates remain intact and unreacted after processing. This was accomplished by coating TiB₂ particles with a C protective coating using chemical vapor deposition. The following conclusions have been determine:

- The reaction between the Ti matrix and TiB₂ particles leading to formation of TiB does readily occur if the TiB₂ particles are not coated.
- The C coating was proven successful in preventing the conversion of TiB₂ particles into TiB for dwell times of 2 h at 1370 °C.
- The C coating showed complete TiB₂ protection in a sample hot pressed at 1200 °C.
- Reaction does occur between the C coating and the Ti matrix leading to the formation of TiC. Near complete conversion was observed in the hot pressed sample at 1200 °C.

This study proves a protective C coating on the TiB₂ particles can prevent the in situ reaction between the Ti matrix and the TiB₂ particles. This allows the superior ballistic properties of TiB₂ and Ti to be utilized in a metal matrix composite that could lead to an improved armor system.

CHAPTER 5 FUTURE WORK

There is still a large amount of future research in this area including the optimization of parameters and many variables are interrelated with each other. Processing parameters such as the hot pressing temperature and dwell time need to be optimized to produce a fully dense material with minimal pores and voids. Additionally an optimal coating thickness should be determined to provide adequate protection of the TiB_2 particles. Too thick of a coating could be detrimental since TiC does not exhibit the ballistic material properties of TiB_2 , however, too thin of a coating could fail to prevent TiB_2 conversion. A thicker coating of up to $10\text{ }\mu\text{m}$ was deposited in this study in order to assure that the particles were completely coated. Another desirable property is that the coating completely converts into TiC . Additional studies producing sample plates made of the composite materials large enough to test the actual ballistic response is desirable. As mentioned, some material properties and tests can be used to help predict the ballistic properties of a material but the actual ballistic protection ability can only be determined from testing a ballistic event.

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VITA

Robert Cody Pack was born in Knoxville, TN to the parents of Robert and Tammy Pack. He is the oldest of three sons: Carter and Carson. He grew up in Anderson County, TN and attended Anderson County High School where he lettered in both football and baseball while also being named his class valedictorian. Cody attended Lincoln Memorial University in Harrogate, TN where he played baseball for four years. He earned his Bachelor of Science degree in Chemistry in May of 2011. After graduation, he accepted an internship at Oak Ridge National Laboratory where he worked for one year. This experience led him to decide to continue his education in material science and engineering. He accepted a Graduate Research Assistant position in the Materials Science and Engineering Department at the University of Tennessee in the fall August of 2012. Cody will earn a Master of Science degree in Materials Science and Engineering in December 2014, and continue his studies for a Doctorate in Materials Science and Engineering.