Properties of titanium matrix composites reinforced with titanium boride powders

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In this project, a revised powder metallurgy method, which contains cold isostatic pressing and hot isostatic pressing, was adopted to refine the microstructure of monolithic titanium. It was also used to manufacture titanium matrix composites. TiH_2 powder was selected as the starting material to form Ti matrix and the reinforcements were sub-micron and nano-metric TiB particles.

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Mechanical properties and microstructures of titanium matrix composites samples in this project, as related to the process parameter, have also been investigated. The density of these samples reached 96% of theoretical one but cracks were found through out the samples after sintering. Fast heating rates during the processing was suspected to have caused the crack formation, since the hydrogen release was too fast during dehydrogenation. Hardness testing of sintered samples was carried out and the value was comparable and even better than that of commercial exhaust valves and titanium composites in literature. Microstructure study shows that the size of reinforcements increased and the size of grains decreased as the increasing amount of TiB reinforcements. And this condition also resulted in the increasing amount of the acicular alpha structure.

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Properties of Titanium Matrix Composites Reinforced with Titanium Boride Powders

By

Fei Yuan (Fred)

Submitted in Partial Fulfillment of the
Requirements of the Degree of Master of Engineering

School of Materials Science and Engineering
Faculty of Science
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Mar 2007

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Abstract

Metal matrix composites can produce mechanical and physical properties better than those of the monolithic metal. Titanium alloys are widely used matrix materials as they can offer outstanding specific strength, corrosion resistance and other advantages over its competitors, such as aluminium, magnesium and stainless steel. In past decades, titanium matrix composites served in broad areas, including aerospace, military, automobile and biomedical industries.

In this project, a revised powder metallurgy method, which contains cold isostatic pressing and hot isostatic pressing, was adopted to refine the microstructure of monolithic titanium. It was also used to manufacture titanium matrix composites. TiH_2 powder was selected as the starting material to form Ti matrix and the reinforcements were sub-micron and nano-metric TiB particles.

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Mechanical properties and microstructures of titanium matrix composites samples in this project, as related to the process parameter, have also been investigated. The density of these samples reached 96% of theoretical one but cracks were found through out the samples after sintering. Fast heating rates during the processing was suspected to have caused the crack formation, since the hydrogen release was too fast during dehydrogenation. Hardness testing of sintered samples was carried out and the value was comparable and even better than that of commercial exhaust valves and titanium composites in literature. Microstructure study shows that the size of reinforcements increased and the size of grains decreased as the increasing amount of TiB reinforcements. And this condition also resulted in the increasing amount of the acicular alpha structure.

Table of Content

1 Introduction

Reinforced materials based on metals have long been of technological significance [1]. There are many types and morphologies of reinforcements used in metal matrix composites (MMCs), principally high-melting-point ceramics, such as SiC or Al_2O_3, in the form of whiskers, particles, and continuous fibers. The major benefits of MMCs over monolithic metal alloys are their higher strength, elastic modulus and crack initiation resistance, but at the expense of toughness. The main purpose in the early research was to achieve improved ductility and toughness in continuously and discontinuously reinforced MMCs without strength sacrificing [1, 2]. Now the cost reduction of the manufacturing process has also become one of the main targets.

Much of the early work on MMCs was mainly on aluminum-matrix alloys. It has been decades that matrices based on titanium alloys have received much interest. Titanium alloys can offer outstanding specific strength and corrosion resistance which are even better than aluminium alloys and steel. To further increase the strength and decrease the cost, a cost-effective powder metallurgy (P/M) method has been proposed in this work to add different sizes of particulate reinforcements into Ti and its alloys to form titanium matrix composites (TMCs). The powder metallurgy process will be described in detail in Chapter 2. For some practical uses, the Ti-B reinforced composites have been used by Toyota Motor Corporation to produce the intake and exhaust valves for their mass-produced high performance family cars [3].

Lots of early research works have been done on the effects of micro-size particulates in titanium alloys matrix. In this work, sub-micron and nano-metric particles are selected as the reinforcements to find out whether pure titanium matrix composites with these reinforcements will have the same, better or even worse mechanical properties than titanium alloys matrix composites with micro-size reinforcements.

In this project, TiH_2 is used as the starting material as it has been shown to have better sinterability and resistance to both elastic and plastic deformation than Ti-started composites [4]. This kind of powder will be described in Chapter 2. Firstly, TiH_2 was mixed with sub-micron and nano-metric TiB_2 particulates, which were the source to form TiB reinforcements in the titanium matrix. This will also be discussed in detail in Chapter 2. The blend was then subjected to cold isostatic pressing (CIP), which can help the green compact to form certain shapes and reach a certain density. Degassing and sintering were carried out after CIPing under the vacuum at the normal processing temperature. Hot isostatic pressing (HIP) would be selected to refine the final products if necessary. All experimental processes were carried out in ANSTO (Australian Nuclear Science and Technology Organization). Detailed experimental approaches will be depicted in Chapter 3. Microstructures and mechanical properties of final composites products, as related to the process parameter, were investigated in UNSW.

According to the designed process, objectives of this project can be concluded into three aspects. Firstly, dehydrogenation process of titanium hydride powders will be investigated to determine the best condition to avoid hydrogen embrittlement in titanium composites samples. Secondly, mechanical properties of manufactured samples needs to be tested to find out whether smaller reinforcements can have better, same or even worse effect on mechanical properties compared with larger ones. The last aspect will be microstructure analysis, which can help to understand how these sub-micron and nano-metric reinforcements strengthen or weaken the composites samples.

2 Background

2.1 Metal Matrix Composites

Metal matrix composites (MMCs) consist of metal reinforced with continuous fibers, whiskers or particles, as shown in Figure 2.1. Metal matrix composites can produce mechanical and physical properties better than those of the matrix metal materials [5]. MMCs combine aluminium, titanium, magnesium or other metal alloys with reinforcements. The main advantages of MMCs are improved mechanical and physical properties that can be adapted to some specific applications, and usually they are lighter than unreinforced metal materials. These MMCs can still maintain these advantages at relatively high temperatures, which depend on different matrix metals [5].

There are two types of metal matrix composites according to the length-to-diameter ratio of the reinforcements. Continuous fiber-reinforced MMCs have reinforcements with a very large length-to-diameter ratio, such as continuous fibers. Discontinuous reinforced MMCs have reinforcements with a small length-to-diameter ratio, such as chopped fibers, particulate and whiskers [1, 5]. Continuous reinforced MMCs generally have mechanical and physical properties superior to discontinuous reinforced ones, because both the modulus and the strength of the continuous reinforcements are almost fully translated into the composites [5].

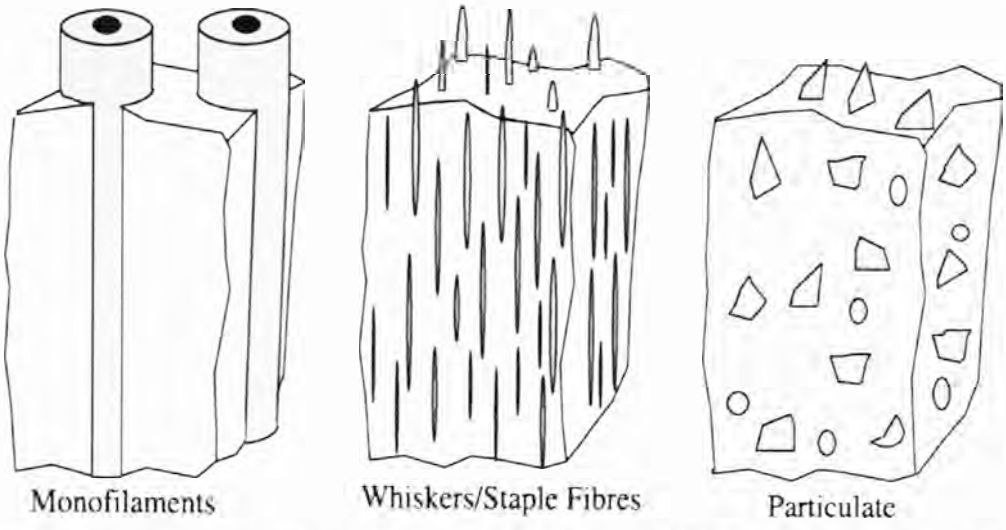


Figure 2.1 A schematic depiction (Clyne and Withers, 1993) of the main MMC systems

In continuously reinforced MMCs, key issues include the processing, ability to produce useful shapes and cost. MMCs with continuous reinforcements can provide the greatest strength and stiffness at premium cost. Landing gear on advanced aircrafts, for example, can use continuously reinforced MMCs to achieve reduced weight and increased environmental resistance. For discontinuously reinforced MMCs, it can also provide increased strength and stiffness, but at higher costs compared with unreinforced metals. They can find applications in lightly loaded, stiffness-critical airframe components where enhanced fatigue or fracture resistance is not necessary. Examples include inertial guidance systems, rudders, escape hatches, and aircraft hydraulic systems [1, 2, 6].

There are some barriers to use MMCs, which include difficulties in machining and the lack of standardization of mechanical property measurements. MMCs with continuous reinforcements have the problem with fiber-matrix compatibility, fiber cost and size, and fiber-coating technology. For MMCs with discontinuous reinforcements, specially designed dies for primary processing is needed. Furthermore, achieving a uniform dispersion of particles and producing a controlled or reduced whisker or particulate size are difficult and processing costs are high. Other constraints include low fracture toughness and poor short transverse mechanical properties [1, 6].

Discontinuous particulates reinforced MMCs have been under development since 1970s. Even that the metal matrix is the minor phase on a volume basis, the kind of MMCs is in the class of particulate reinforced MMCs [2]. These materials have raised lots of attention since some cost-effective processes began to be widely used. And the interest has resulted in MMCs as advanced materials for a range of applications in the automotive, aerospace, military, recreational and other fields in recent decades. Over the last 30 years, there have been many successes, failures and challenges with particulates reinforced metal matrix composites. Shortcomings include that they are not homogeneous and are sensitive to the properties of the constituent, interfacial properties, the geometric shape of the 3-D reinforcement [1, 5].

Titanium alloys can offer outstanding specific strength, corrosion resistance and other advantages over its competitors. Since the beginning of titanium matrix composites (TMCs) in the 1980s, considerable development and progress have occurred toward their applications in aircraft engines, airframe structures, military, automobile and biomedical industries [5]. The automobile industry is very keen to replace stainless steel parts in the cars with titanium ones, providing that the cost of the latter is comparable to that of the stainless steel. 304 and 400 series stainless steel are the main competitors to titanium in the industry [7].

There are lots of advantages of using Ti composites, as have been found recently by Saito [3] for engine valves. The engine with Ti composite pistons valves can have a 40% lighter valve weight and 16% lighter valve spring weight when compared with the conventional steel-valve engine. As a result, the maximum revolutions increased by 700 rpm, and the noise in the high-revolution range decreased by 30%. Also, the reduction of friction in these Ti composites reduces camshaft driving torque by 20%, with high performance and low fuel consumption. Figure 2.2 shows an example of the Altezza family car of Toyota Motor Corporation which equipped with Ti composites engine valves and the typical intake and exhaust valves are shown in Figure 2.3.

Figure 2.2 Altezza family car of Toyota Motor Corporation

Figure 2.3 Intake and exhaust valves made of TMCs by Toyota Motor Corporation [3]

Being equipped with titanium exhaust systems, the lifetime of the car can last 12~14 years while the one being equipped with stainless steel must be replaced after 7 years [8]. The lightweight advantage of titanium over stainless steel in this application also benefits the use of titanium. A typical car's exhaust system weighs about 20kg and weight reductions (40-50%) have been reported when titanium in used in place of steels [7, 9, 10]. This will result in a 9 kg reduction in car body weight and this reduction can be expected to give a fuel consumption reduction of about 80L over a typical 200,000 km lifespan of the car [7]. As a result, more than 500,000 P/M TMC valves have been put into the market since 1998

[3]. This represents the biggest usage of Ti composites in non-military applications. So, it has been demonstrated that this class of composites is technically feasible material and is ready to deliver many outstanding benefits.

2.2 Titanium and Titanium Alloys

2.2.1 Titanium

Titanium, with a lustrous, iron-like appearance, is used in the manufacture of aircraft and spacecraft parts, chemical equipment and biomedical equipment such as bone replacements. Pure titanium melts at about 1670°C, and has a density of 4.51g/cm^3, compared with approximately 7.8g/cm^3 for steels and superalloys. Titanium is twice as resilient to mechanical stress (30kg/mm^2) with an elastic modulus of 1.18×10^4kg/mm^2, a Brinnell hardness of 120kg/mm^2, a fatigue limit of 33kg/mm^2, as iron. So it is ideal for using in the high operation temperatures, especially where large strength-to-weight ratios are required [11].

The yield strength to density ratio of titanium alloys is considerably higher than that of steels, aluminium and magnesium alloys [12, 13]. Compared even to platinum, titanium is still a superior metal because of its chemical stability, and to other metals because of its ductile qualities. Titanium, which has the lowest friction constant, loses heat more rapidly than steel, and is therefore well suited to high-temperature applications where frequent heating is required. Titanium is also non-magnetic, which is an advantage for high speed processing. Furthermore, because of titanium's corrosion resistant even in sea water and non-ionic properties, it is often used for prosthetic devices and orthopaedic implants, since tissue grows on titanium quite readily [11, 12].

As an example [6], reasons for using titanium for aircraft applications include:

1) Weight savings. In various applications the strength to weight ratio of the titanium can exceed that of stronger but heavier steel alloys and lighter but weaker aluminium alloys. The consequent weight savings achieved by using titanium instead of the competing alloys can be significant.

2) Operating temperature. Titanium is most commonly used when the operating temperature exceeds about 135°C, which is the normal maximum operating temperature for aluminium. These conditions exist in the nacelle, auxiliary power unit area, and wing anti-icing systems for airframe structures. Steel and nickel-base alloys are obvious alternatives, but they have a density of about 1.7 times that of titanium.
3) Corrosion resistance. Excellent corrosion resistance enables titanium to be used in most applications without the addition of protective coatings.
4) Composite compatibility. Titanium has found significant use in contact with polymeric composite components because titanium is more galvanically compatible with carbon fibers than aluminium and has a relatively good match of coefficients of thermal expansion.

Titanium passivates at low temperatures and becomes almost completely inert to most mineral acids and chlorides. At high temperatures, titanium oxidizes very quickly and its properties can be greatly altered by the absorption of oxygen interstitials from the air. Heating the titanium in the air will result not only in its oxidation but also in the dissolution of oxygen and nitrogen in the surface layers of titanium, which will cause solid-solution hardening of the surface. The thickness of the "air contaminated layer" depends on the temperature as well as the dissolution time. This layer can be removed by machining or other methods prior to using the alloy because the presence of the air contaminated layer reduces the fatigue strength and ductility [13]. So, all high temperature processes with titanium even as low as 600°C must be carried out in an inert atmosphere or the vacuum. Furthermore, titanium can catch fire and cause severe damage in circumstances where it rubs against other metals at elevated temperatures, as shown in Figure 2.4. This is the limit for its application in the harsh environment of aeroengines, and it should be used in regions where the temperature does not exceed 400°C [14].

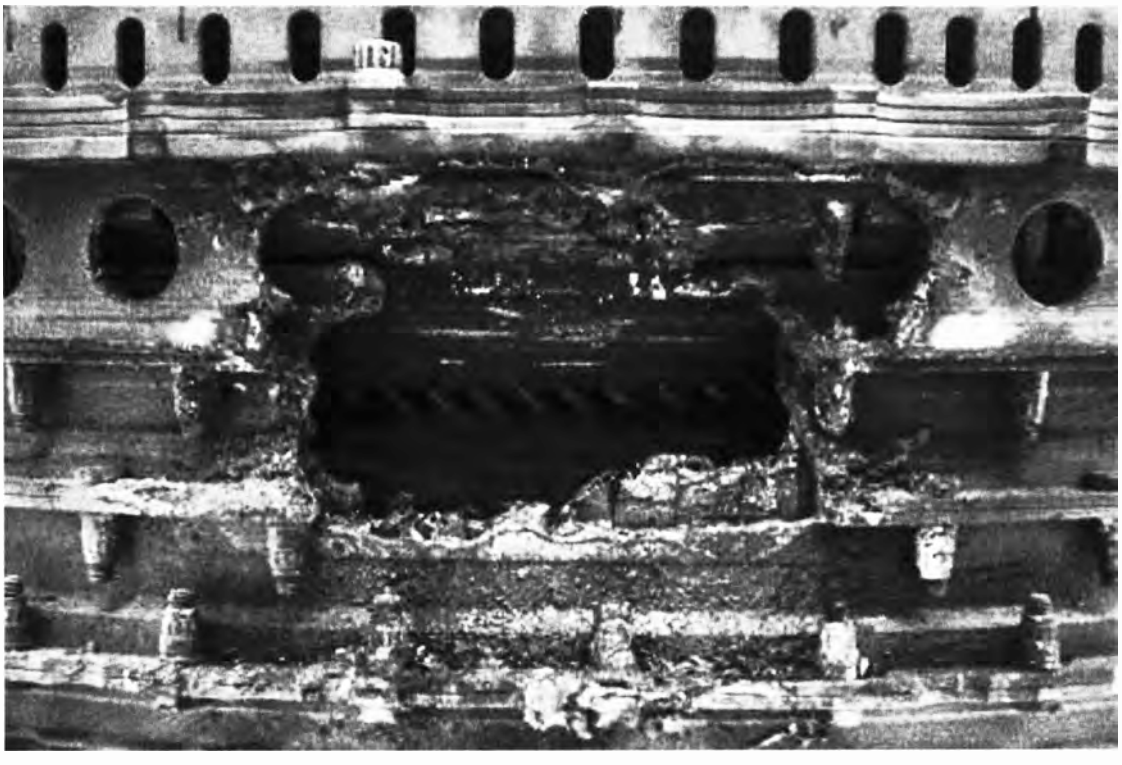


Figure 2.4 Consequences of a titanium caused fire in an aeroengine. Nickel alloy blades have been burnt away [14].

Titanium metal is used widely in both its commercially pure (CP) form and in a range of alloys that optimize various properties as required for the intended use. With highly weldable and formable ability, CP titanium generally has lowered tensile and yield strengths than its alloys [7]. A brief introduction on titanium alloys will be made in the next section.

2.2.2 Titanium Alloys

Pure titanium exists in two allotropic forms, α-Ti, which is hexagonal close-packed (h.c.p) and exists below 882°C, with a c/a ratio of 1.587, which is much smaller than the standard c/a ratio of 1.633. Thus, slip system is possible on the pyramidal, prismatic and basal planes in the close–packed directions, as shown in Figure 2.5. The other form of the pure titanium, β-Ti, is body centered cubic (b.c.c), exists above 882°C and remains stable to the melting point [13, 14].

The temperature at which these phases are stable can be altered by alloying. An element which raises the temperature at which alpha is stable is known as an alpha stabilizer and has a high solubility in the alpha phase. An element which lowers the temperature at which beta is stable is a beta stabilizer and has a high solubility in the beta phase. The temperature of the β/(α-β) phase boundary of an alloy is commonly known as the β-transus temperature and the α/(α-β) temperature is known correspondingly as the α-transus temperature [15]. The phase diagrams of titanium alloys are shown as Figure 2.6.

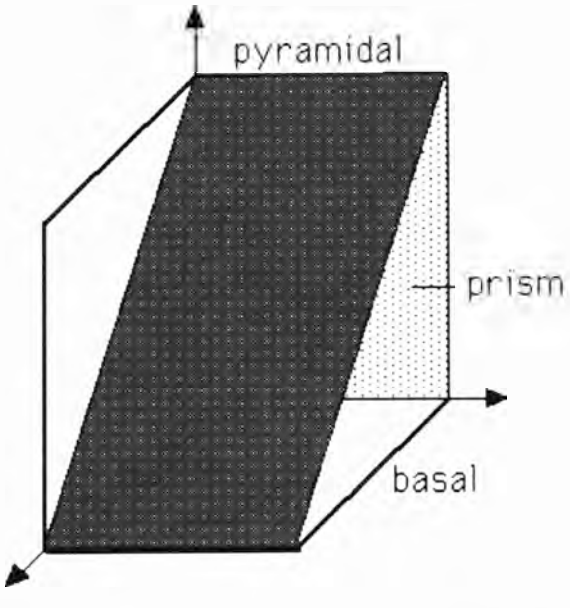


Figure 2.5 The slip planes in titanium [14].

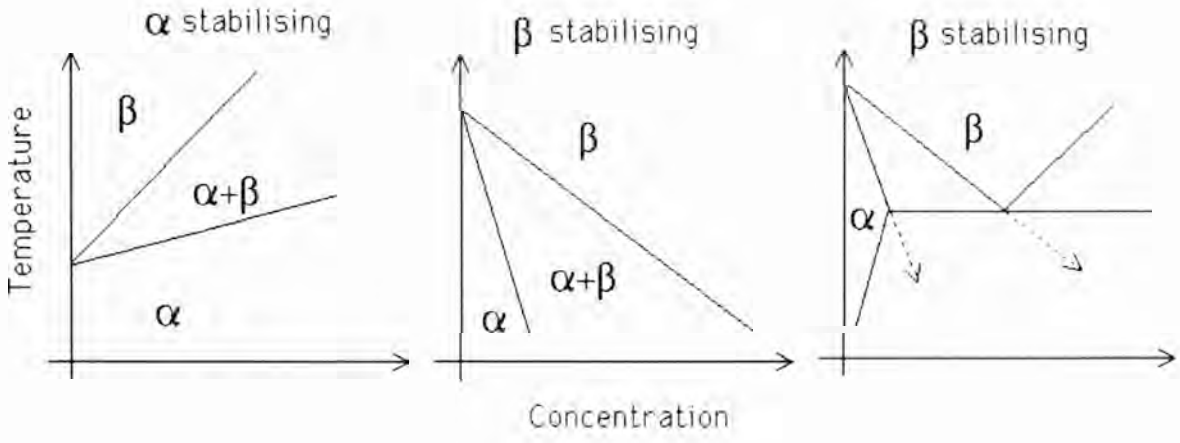


Figure 2.6 Phase diagrams of titanium alloys [14].

A. Alpha and Near Alpha Alloys

Oxygen, nitrogen and carbon are three important alpha stabilizers. They are important because they lower the ductility of titanium and can be rapidly absorbed by titanium when the metal is hot. Aluminium, another alpha stabilizer, has significant solubility in both α and β phases, so it has a strong solid-solution hardening effect on titanium and strengthens both phases, but it can reduce its ductility. Tin strengthens the Ti without a significant loss in ductility, and it initially lowers the β-transus temperature then raises it, thus tin is categorized as both a beta stabilizer and an alpha stabilizer, depending on the composition. All of these elements harden and solution-strengthen α alloys [13, 15, 16].

Because of the absence of ductile-brittle transformation, which is a property of b.c.c structure, alpha alloys are always used in cryogenic temperature. So, alpha alloys containing no β-stabilizers cannot be strengthened by heat treatment. They are usually annealed or recrystallized to remove residual stresses induced by cold working [16].

Alpha alloys are generally more resistant to creep at high temperature than β or α-β alloys. They have good weldability because they are insensitive to heat treatment. But they have poorer forgeability and narrower forging temperature ranges than β or α-β alloys,

particularly at temperatures below the β transus temperature [13, 16]. In total, alpha alloys have good strength, toughness, creep resistance, weldability but poor forgeability.

Alpha alloys that contain small additions of β stabilizers are categorized as "near-α" alloys. They behave more like conventional α alloys than α-β alloys. But they can be strengthened by heat treatment. Near alpha alloys have higher room temperature tensile strength than the fully alpha alloys and show the greatest creep resistance among all titanium alloys at above 400°C [13].

B. Beta Alloys

There are two general forms of beta stabilizers.

1) Elements which form complete solid solutions in the beta field are known as isomorphous beta stabilizers, such as zirconium, molybdenum, tantalum, vanadium and niobium. These elements are isomorphous with β at high temperatures and form α-β equilibrium phases at ordinary temperatures. Zirconium, one of these elements, is completely soluble in beta and alpha titanium.

2) Elements which have limited solution in the beta field and show beta decomposing eutectoidally are known as eutectoid formers. These elements are chromium, iron, copper, nitrogen, palladium, cobalt, manganese and hydrogen [13, 15].

All these beta stabilizers have limited solubility in alpha phase. They impart solid-solution hardening to the beta phase and hardly affect alpha phase. So, a combination of alpha and beta stabilizers is added into the two-phase alpha and beta alloys to strengthen both phases [16].

Beta alloys actually are metastable, because cold work at room temperature or heating to a slightly elevated temperature can cause partial transformation to α phase. The beta to alpha transformation in pure titanium occurs very easily and cannot be suppressed by rapid quenching. So it is widely believed that the transformation is a diffusionless martensitic

transformation, rather than the one that is diffusion controlled. In appropriately fine dispersions of alpha titanium can also strengthen beta. Control of the beta decomposition is important because a wide variation in properties can be achieved [13, 16]. On cooling, beta can decompose to form α in a variety of morphologies. On quenching, beta can form martensite, a supersaturated alpha, in alloys whose content is less than that required to retain the beta. It can also form a complex hexagonal transition phase known as omega. Omega hardens and embrittles beta, and commercial alloys are not heat treated to produce omega [15].

Beta alloys are susceptible to a ductile-brittle transformation and therefore unsuitable for low-temperature applications. They are characterized by high hardenability, with β phase completely retained on air cooling of thin sections or water quenching of thick sections. They have excellent forgeability and can be cold formed more readily than high strength α or α-β alloys. After solution treating, they are aged at temperature ranging from 450°C to 650°C to partially transform the β phase to α phase [13, 16]. So, advantages of β alloys are that they are cold rollable and have high hardenability, excellent forgeability, good ductility and toughness and excellent formability in the solution treated condition. Their limitation is often the temperature capacity, generally due to poor creep resistance and oxidation behavior. The β-21S (Ti-15Mo-2.7Nb-3Al-0.2Si) overcomes these common shortcomings of metastable β alloys [16].

C. Alpha-Beta Alloys

Alpha-beta alloys contain one or more α stabilizers plus one or more β stabilizers. It has been found in experiments that alloys containing both the alpha and beta phase together produce the highest strengths. To obtain strengthening, these alloys are quenched after solid solution treating in the alpha-beta field. They are subsequently aged at a lower temperature to produce hardening [13, 16].

The form in which alpha exists after quenching from the solution treatment temperature affects ductility. If alpha forms on cooling from the beta field into the α-β field, there is a tendency to form a continuous network of alpha around the beta grain boundaries, and within the beta grains alpha precipitates in Widmanstatten or acicular distribution. An acicular α structure can exhibit superior creep properties, higher fracture toughness values, superior stress-corrosion resistance, lower crack-propagation rates and slightly lower tensile and yield strengths at room and elevated temperature for equivalent heat treatment [16]. Other microstructures, such as equiaxed or duplex structures, exhibit higher ductility and formability, higher threshold stress for hot-salt corrosion, superior low-cycle and high-cycle fatigue properties at room and elevated temperatures, slightly higher tensile and yield strengths at room and elevated temperature for equivalent heat treatment [16].

Alpha-beta alloys retain more β phase after solution treatment than do near-α alloys and the amount depends on the quantity of β stabilizers present. They can be strengthened by solution treating and aging. Solution treating is done at a temperature high in the two phase α-β field and is followed by quenching in water, oil and other suitable quenchant. As a result, the β phase present at the solution treating temperature may be retained or may be partly transformed during cooling by either matensitic transformation or nucleation and growth. Solution treatment is followed by aging, which is carried out between 480 and 650°C, to precipitate α and produce a fine mixture of α and β in the retained or transformed β phase. Solution treating and aging can increase the strength of α-β alloys 30% to 50%, or more, over the annealed or over-aged conditions [16].

Alloys low in β stabilizers, such as most widely used Ti-6Al-4V, have poor hardenability and must be quenched rapidly to acquire significant strengthening. So, alloy composition, solution temperature and aging condition must be carefully selected to produce the desired mechanical properties in the product [16].

2.3 Titanium Hydride Powder

2.3.1 Introduction

TiH_2 powder is used as the starting material in this project.

Titanium hydride (TiH_2) is a grey powder with face centered cubic crystals and a specific density of 3.8g/cm^3. In the temperature range of 300-750°C, titanium hydride dissociates into Ti and H_2 gas. The reaction is reversible in the same temperature range [11].

Titanium has a high affinity to hydrogen and the hydrogen absorption transforms the titanium from metal (h.c.p., α-phase) to hydride (f.c.c., δ-phase) [11]. Among the hydrides of Ti, TiH_2 is extremely brittle and can be pulverized to nano-crystalline form by mechanical milling for a short period of time. The hydride can then be dehydrogenated to form Ti powder which then can be consolidated to produce fine grained Ti components [17]. It is believed the titanium particles after dehydrogenation become easily fused for two reasons. Firstly, particles' surface has just been activated due to the hydrogen evacuation and secondly the heat $\triangle H$ released increases the local temperature at the interface between the particles to a fusion level [11]. When the Ti-H bond is broken, an amount of heat is produced. The heat can increase the temperature of the titanium particles to a fusion level, which can generally help to lower the sintering temperature from normal 1200-1300°C to 1100°C [11].

2.3.2 Dehydrogenation of TiH_2 Powder

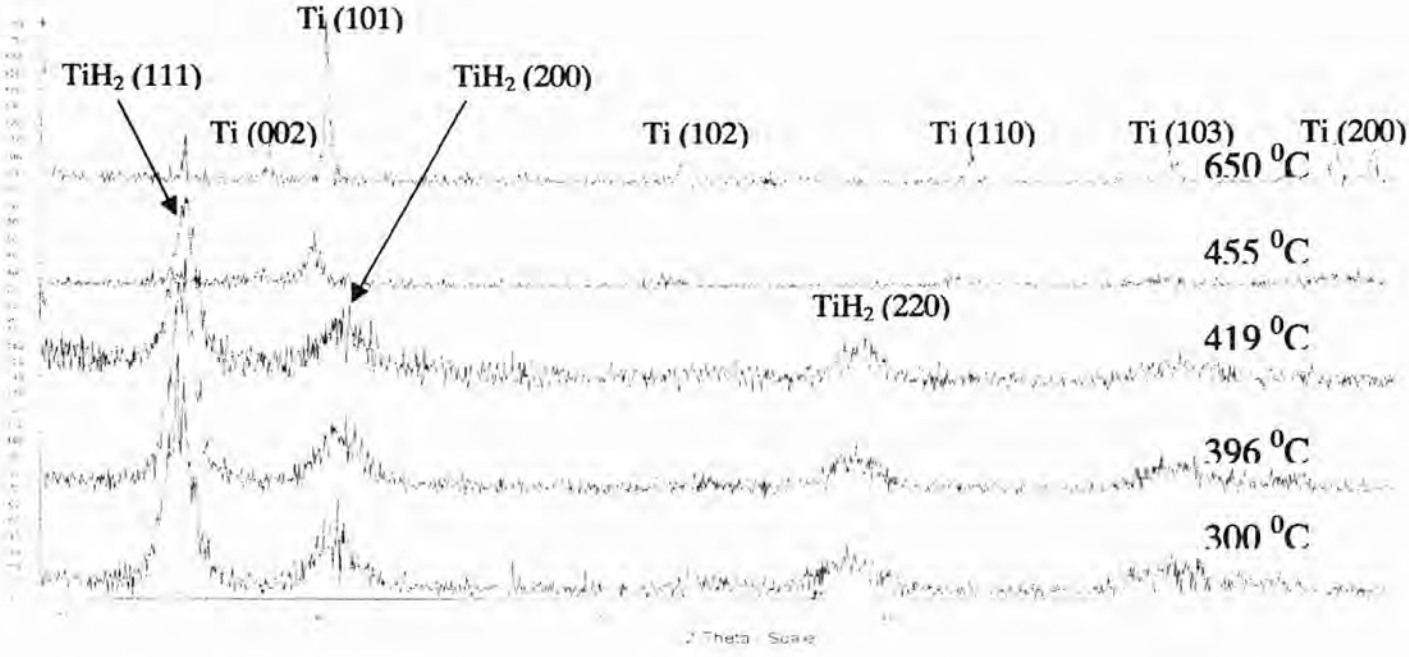


Figure 2.7 XRD patterns of TiH_2 samples heated up to different temperatures under vacuum atmosphere [17]

According to Figure 2.7 and some previous works [11, 18], most of the hydrogen will come out between 400°C and 650°C. A large release of hydrogen in a short time may pose a risk of explosion and it also affects adversely the quality of the final product due to hydrogen cracking. Therefore the hydrogen release rate has to be regulated [19, 20]. This is one of the objectives of this work, to identify the best dehydrogenation conditions for this.

2.3.3 Advantages and Applications of TiH_2 Powder

TiH_2 powder is used as the starting material in this project as it has many advantages compared with pure titanium. Firstly, hydrogen is a unique alloying element for titanium, because it can be introduced into the metal to form solid solutions or stoichiometric compounds by exposure to the gas at elevated temperatures and removed by vacuum annealing. The presence of hydrogen in Ti can enhance processability including cold and hot working, machining, powder production by hydride-dehydride (HDH) process, and microstructures control to improve mechanical properties [17]. Secondly, TiH_2 is more cost effective than CP titanium in the fabrication, and it can have low adherence with the metal die during the fabrication [3]. Thirdly, the oxygen content of TiH_2 is also lower than CP titanium, and a low O_2 content is the fine-sintering requirement during the fabricating. Furthermore, titanium hydride has a better sinterability, especially in pressureless vacuum sintering. And it has been shown in the previous work that TiH_2-started composites with TiC reinforcement have a better resistance to both elastic and plastic deformation than Ti-started ones [4].

Titanium hydride has previously been used chemically for producing silicides, nitrides and borides as a catalyst in hydration of organic compounds and to obtain extremely pure hydrogen [11]. In general, TiH_2 is widely used as excellent raw materials for the sintering of parts, raw materials of HDH powder, TiC and TiN, thermal spray coating materials, synthesizing material for alloys, hydrogen source for foaming metal, material of reduction and hydride reservation, bonding materials and inter-metallic compounds [18].

2.4 Sub-micron and Nano-metric Reinforcement

2.4.1 Titanium Boride Reinforcement

Titanium boride (TiB) is selected as the reinforcement in this project. Figure 2.8 shows the Ti-B binary phase diagram [21], and there are three intermetallic compounds: TiB, Ti_3B_4 and TiB_2 in the diagram. TiB has been found to be the most appropriate reinforcing phase for TMCs because it tends to form long whiskers and offers a clear crystallographic orientation relationship with the titanium matrix. In addition there is no brittle intermediate phase formation between Ti and TiB [22, 23].

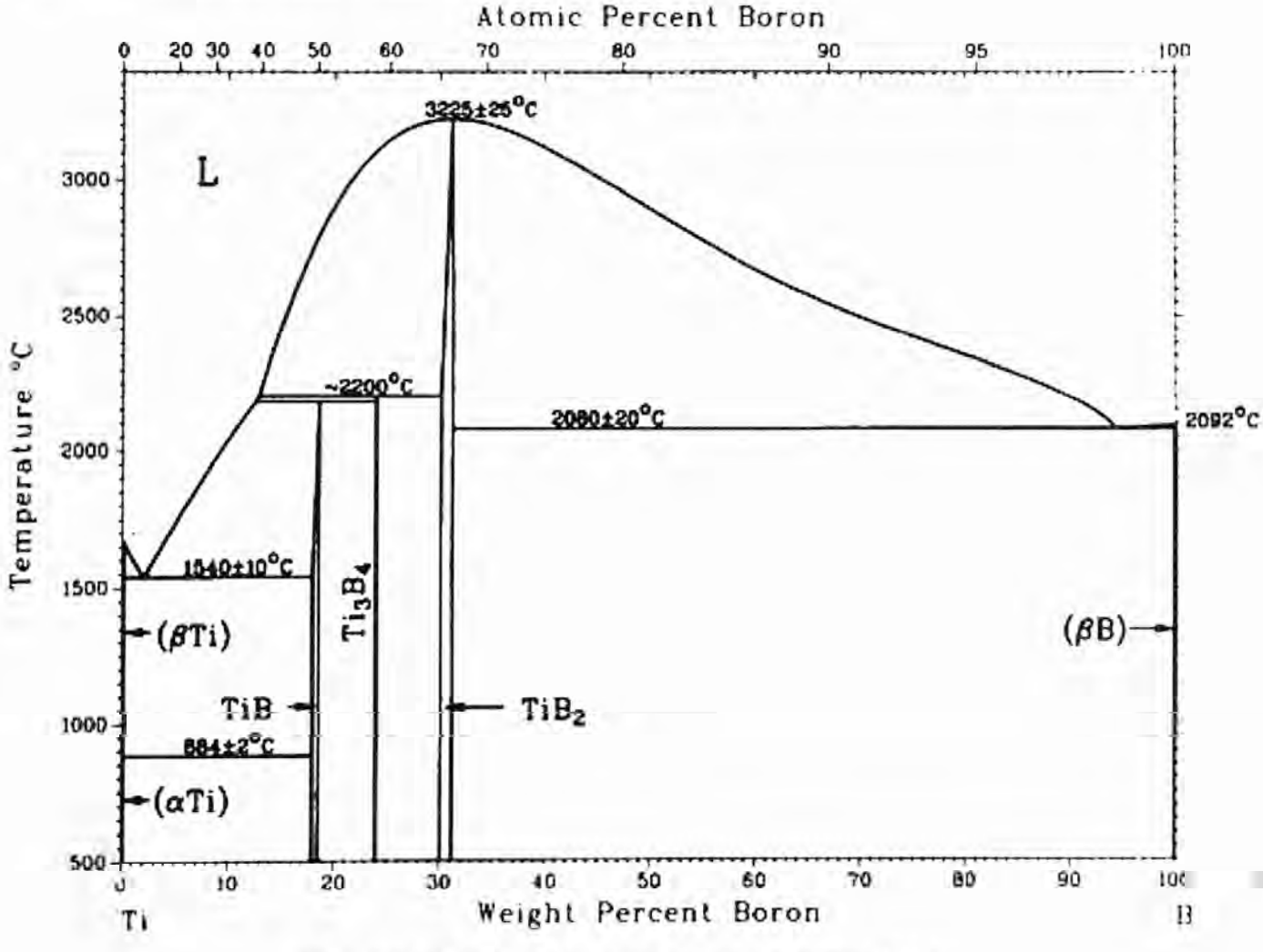


Figure 2.8 The Ti-B binary phase diagram [21]

Relatively small boron additions to conventional titanium alloys provide important improvements in strength, stiffness and microstructural stability. Because boron is insoluble in Ti at all temperatures of interest, the intermetallic compound TiB is formed for even very small boron additions. The density of TiB is nearly the same to that of Ti alloys, but its stiffness (~500GPa) is over 4 times higher than conventional titanium alloys (~110GPa), so it can offer significant improvements in stiffness, tensile strength, creep and fatigue properties [23, 24]. Since TiB is in thermodynamic equilibrium with titanium alloys, so that there are no interfacial reactions to degrade properties with exposure at elevated temperature. Furthermore, TiB has a similar coefficient of linear expansion ($8.6\times10^{-6}/^{o}C$) as that of titanium ($9.7\times10^{-6}/^{o}C$), so that residual stresses can be nearly eliminated [3, 24].

The whisker-like TiB has an aspect ratio of about 10:1, so isotropic properties are obtained when TiB particles are randomly oriented. But intentional alignment of the TiB through extruding or rolling can help produce higher strength and stiffness along the direction of TiB alignment [24].

In 1998, Toyota Motor Corporation adopted intake and exhaust valves made of titanium alloys based alloys for engines of its Altezza [3]. Both valves were made through P/M method. For the reinforcement, TiB was used with a size range of micron. Among lots of the reinforcements, such as TiC, SiC, TiB_2, B_4C, Si_3N_4 and TiN, TiB is outstanding in all physical and mechanical properties, which can be concluded from Figure 2.9 [3]. TiB is very stable in titanium alloys, but it is unstable by itself and cannot be treated in powder form. So, pure boron, boride powders or titanium diboride (TiB_2) must be used as the boron source. TiB_2 is selected in this work as the boron source for the in-situ formation of TiB in the titanium matrix. It reacts with titanium powder during sintering to form thermodynamically stable TiB particles throughout the titanium alloy matrix with a highly crystallographic coherency at the inter-phase boundary [3].

Particle	Knoop Hardness (GPa)	Young's Modulus (GPa)	Coefficient of Linear Expansion*	Maximum Solubility [Matrix] [Particle] (at.%)	Estimation
TiB	28.0	550	8.6	<0.001 1.0	Excellent
TiC	24.7	460	7.4	1.2 15.0	Passable
TiN	24.0	250	9.3	22.0 26.0	Failure
SiC	25.0	420	4.3	Unstable in Ti alloy	Failure
Si_3Ni_4	14.7	320	3.2	Unstable in Ti alloy	Failure
TiB_2	34.0	529	6.4	Unstable in Ti alloy	Failure
B_4C	27.5	449	4.5	Unstable in Ti alloy	Failure
Al_2O_3	22.5	350	8.1	Unstable in Ti alloy	Failure

Figure 2.9 Mechanical properties of different reinforcement particles for the TMCs (coefficient of linear expansion of titanium alloy is around 9×10^{-6} K^{-1}) [3]

2.4.2 Nanotechnology in this Project

Nanotechnology has attracted broad attention of many materials scientists in the modern world. This term is used to cover the design, construction and utilization of functional structures with at least one characteristic dimension in nanometers, which ranges from 10^{-9} m to 10^{-7} m (1-100nm). Such materials and systems can be designed to exhibit novel and significantly improved physical, chemical and biological properties and processes as a result of the limited size of their constituent particles or molecules [25].

Nano-particles may also be quasi-crystalline. Such quasi-crystals are generally only stable at the nanometers or, at most, the micron scale. Nano-particulates may be present within another medium, such as nanometer-sized precipitates in a surrounding matrix material. The precipitates will have a specific morphology (spherical, needle-shaped or plate-shaped) and may possess certain crystallographic orientation relationship with the atomic arrangement of the matrix depending on the coherency of the interface, which may lead to coherency strains in the particle and matrix [25].

Nanometric particulates exhibit many attractive and special properties and are now readily available. Some research work on the fabrication of nanometric particulates reinforced aluminium matrix composites (AMCs) via powder metallurgy routes have been done by Chan's group [26], and they have got some attractive and challenging results, as shown in Figure 2.10. It can be concluded from the diagram that with a small volume fraction of nano-size Al_2O_3 reinforcement, AMCs can have the same or even better mechanical properties than those of AMCs with 10% micron SiC particulates reinforcement. Accordingly it may be more cost-effective to use a small amount of reinforcement to achieve the strengthening of the alloys.

In this project, sub-micron and nano-metric particulates are used as the source to form reinforcements. The effect of difference in coefficient of thermal expansion between the matrix and the reinforcement can be nearly eliminated using small particles, because thermal mismatch can be largely accommodated by the micron matrix materials. According

to this, other kinds of nano-reinforcements can also be considered, such as titanium carbide (TiC) and titanium nitride (TiN). Examination on the final products will be carried out to make sure whether nanotechnology benefits their mechanical properties or not, and some strengthening mechanism will be concluded through different microstructures of the TMCs if available.

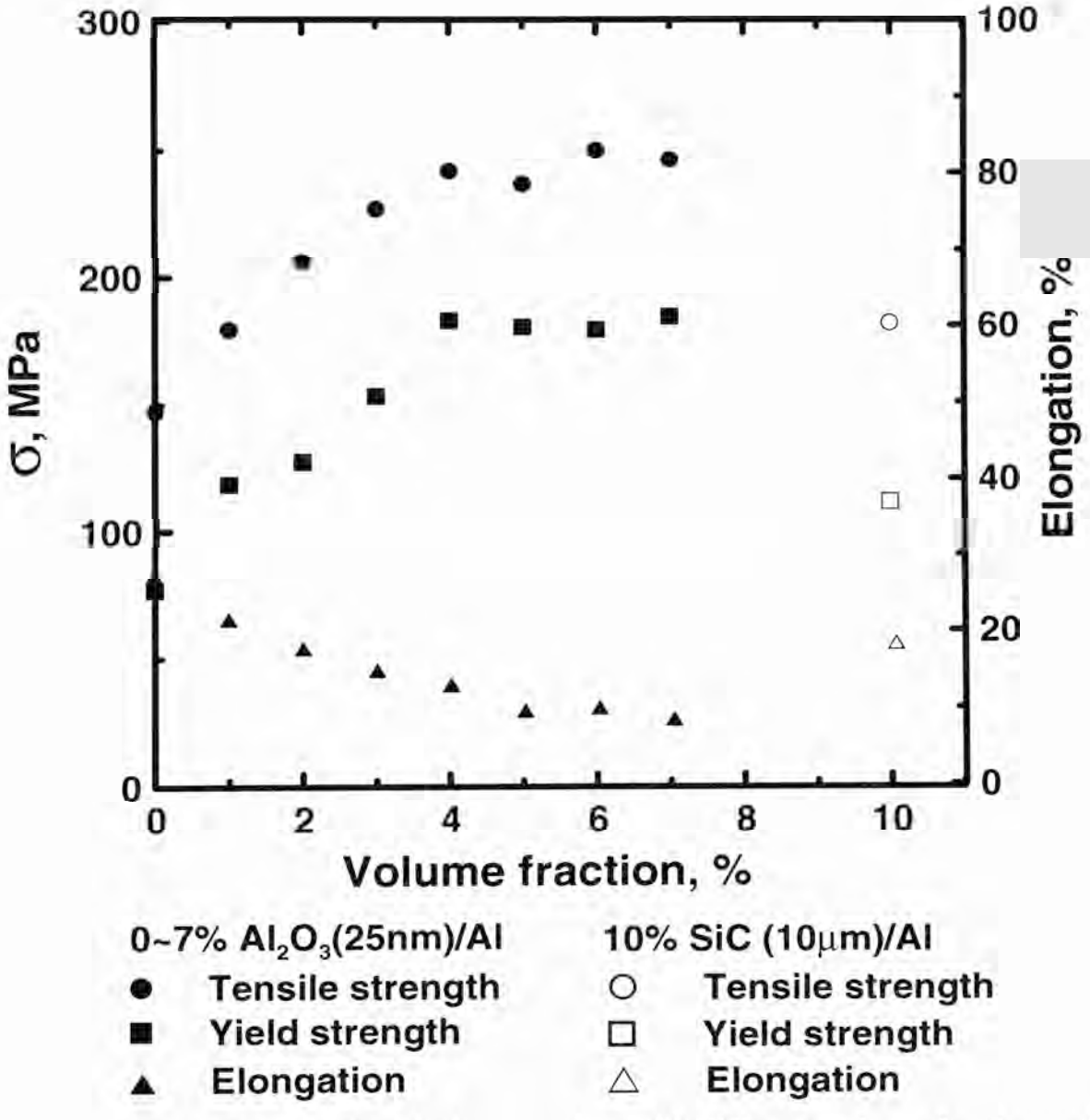


Figure 2.10 Mechanical properties of Al composites with different volume fraction and size of the reinforcements [26].

2.5 Powder Metallurgy Processes

2.5.1 Conventional P/M Process

Discontinuously reinforced metal matrix composites can be prepared by powder metallurgy (P/M) processing. P/M composite fabrication includes the choice of reinforcement type, size and level, matrix chemistry, matrix powder size and shape, followed by the selection of blending and degassing procedures, and finally compaction temperatures and pressures. These choices are interconnected and all influence the composite's mechanical and physical properties [27]. Figure 2.11 shows the general P/M process used in the fabrication of MMCs.

The P/M route has the advantage of reducing the interaction between the ceramic reinforcement and the matrix through semisolid and solid-state processing. Other attractive features include [27]:

1) Combining various matrix reinforcements within the same composite.
2) Utilizing nonequilibrium matrix alloys produced by rapidly solidification.
3) Achieving high reinforcement volume fractions.

However, the P/M route does have disadvantages. These can be concluded as [27]:

1) Its relative high cost when compared to solidification processing.
2) Its relative complexity.
3) Requirement of safety precautions because of many highly reactive powders.

In this project, P/M method such as mechanical alloying and blended elemental powder processing are chosen to produce TMCs with different compositions that would be impossible to achieve by other conventional processing.

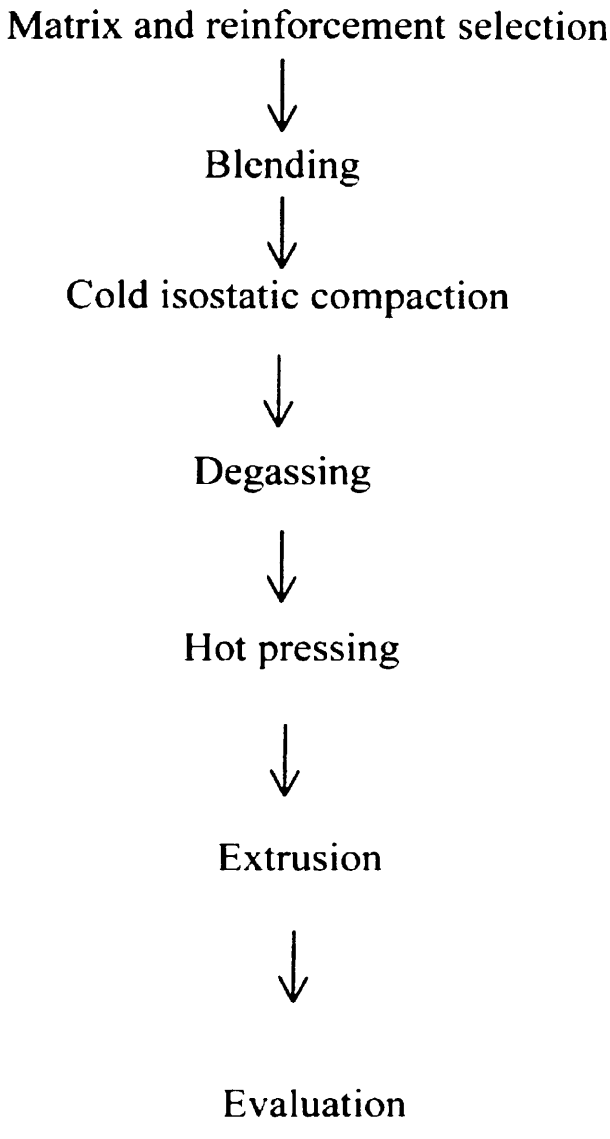


Figure 2.11 P/M route used in the fabrication of MMCs [27].

2.5.2 Revised Process in this Project

As a reference of this project, Toyota Motor Corporation adopted a cost-effective P/M process to manufacture their TMCs valves. The process is shown in Figure 2.12.

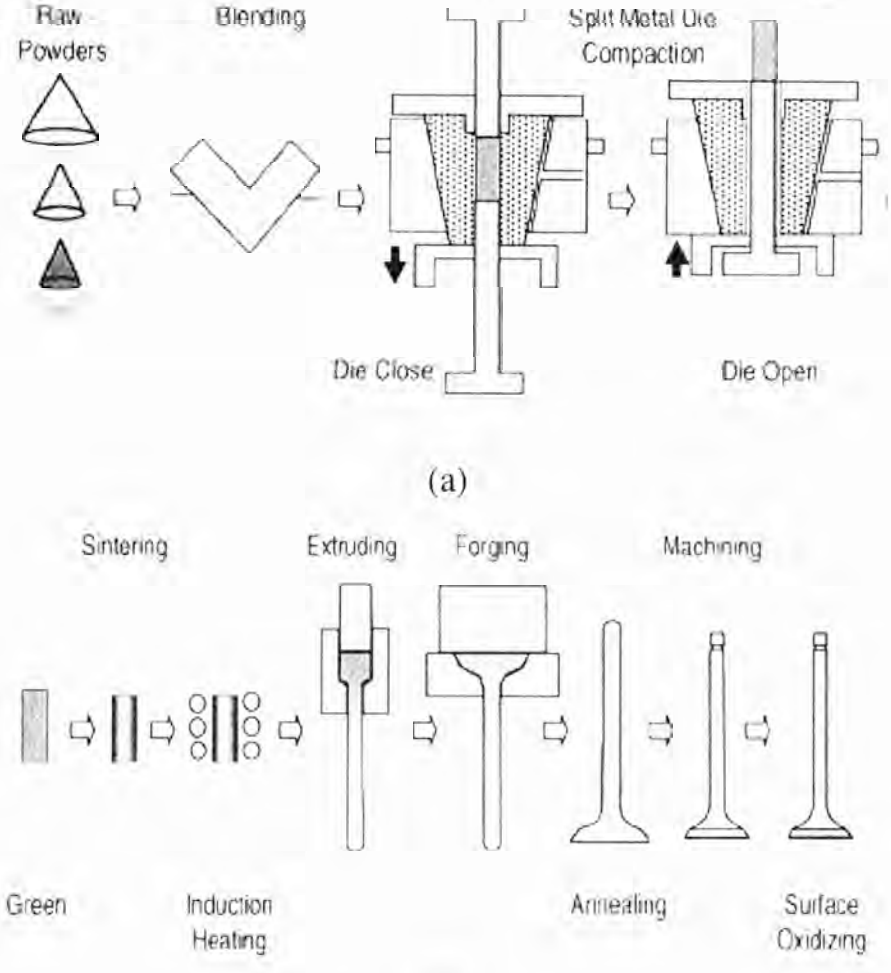


Figure 2.12 The processing steps for the blended elemental TMCs valve production: (a) Powder Mixing and Cold Pressing. (b) Sintering and Post-sintering Processing [3].

All starting materials were mixed in a high energy ball mill. After metal die compaction into a column of about 16mm×40mm at a pressure of 490MPa, vacuum sintering of samples at 1300°C was conducted upon the compact and a sintered billet was prepared for hot forming. Induction heating was used next at around 1200°C to extrude the valve and followed by hot forging for the valve face. Annealing and oxidation treatment were performed after correction of bending of the stem part [3].

In this project, powder mixing, CIPing, degassing and HIPing consist of the fabrication process. CIPing and HIPing are employed during the process in order to save manufacturing steps and improve mechanical properties of TMCs. Steps saving include combining the sintering into HIPing and excluding extruding and forging processes.

Cold isostatic pressing applies pressure from multiple directions for achieving greater uniformity of compaction and thus high quality parts and increased shape capability, compared to uniaxial cold pressing. There are two methods of isostatic pressing. In wet-bag isostatic pressing, powder is encased in a rubber mold which is immersed in a liquid which transmits the pressure uniformly to the powder. In dry-bag isostatic pressing, rather than immerse the entire mold in a fluid, the mold itself is built with internal channels into which high-pressure fluid is pumped [28].

Degassing process in the experimental procedure is the dehydrogenation process of titanium hydride powders which has been described in Chapter 2.3.

Hot isostatic pressing is used when great uniformity is required, and where net-shape production leads to economical advantages, such as titanium alloys for aerospace applications and complex ceramic parts. It is a manufacturing process used to reduce the porosity of metals. This improves the mechanical properties and increases workability. The process is analogous to CIP. The apparatus in use is a high-temperature furnace enclosed in a water-cooled autoclave capable of withstanding high pressures and providing a uniform hot-zone temperature (up to 2000°C). And the pressurization gas is argon or helium. An inert gas is used, so that the material does not chemically react. The chamber is heated, causing the pressure inside the chamber to increase. Due to the presence of the gas, pressure is applied to the material from all directions. The sintering-HIP, which is a version of the process, achieves improved strength and wear resistance of some ceramics or ceramic composites materials for cutting tools and other applications [28].

3 Experiment Approaches

3.1 Materials Used in this Project

Titanium alloys exhaust valves under testing were purchased from Toyota Motor Corporation.

The TiH_2 powders were produced by AG Materials Inc., Taiwan, and the TiB_2 powders were commercial from Dandong, China.

For the starting material, only powders having a particle size larger than 10 micron will be used, as it has been demonstrated that the oxygen content of Ti parts increases dramatically with small Ti powders [29]. The mean size of the titanium hydride powders used in this project was 10.39 μm and the purity was larger than 99.65%, which were reported by AG Materials Inc., Taiwan.

The mean size of the titanium diboride powders used in this project was 1.37 μm and the purity was larger than 94%, which were reported by Dandong Chemical Engineering Institute, Dandong, China.

Some testing results of the powders will be described in Chapter 4.

3.2 Processing, Facilities and Properties Evaluation

All manufacturing processes of TMCs in this project were carried out in Australian Nuclear Science and Technology Organization (ANSTO). All testing of samples were carried out in UNSW.

The production of Ti matrix composites reinforced with sub-micron particles consisted of powder mixing, cold isostatic pressing (CIP), degassing (dehydrogenation), and sintering hot isostatic pressing (HIP). CIP is employed here as it can pre-shape the blend before it is put into HIP process. Also the density of the green body can reach about 60%-70% of the theoretical density, comparing with the normally 20%-30% of cold uniaxial pressing.

The raw powders TiH_2 and TiB_2 were mixed in a turbular mixer, which was designed by ANSTO for general use and shown in Figure 3.1, for 30 minutes at room temperature. The amounts of reinforcement added are 0%, 1%, 3% and 5%, according to the 3% (All units are in weight percent) of titanium diboride added into the titanium composites valves manufactured by Toyota Motor Corporation [3].

Figure 3.2 shows the AIP CP360 Cold Isostatic Press machine used in this work. The blend was put into the rubber mold, which is soft and can avoid apparent deformation during the processing, at the room temperature and formed the cylinder-like green compact at 400MPa for 2 minutes. The pressure medium was water-soluble oil. The packing density of TiH_2 was calculated to be 1.6 g/cm^3, so the total mass of powders used in the mold was 165g.

The green compacts after CIPing were then put into the alumina crucible surrounded by Ti metal swarf, which is used as the separation medium of different samples and to prevent the gas contamination, because of its large surface area and reactive characteristics. Facility used here was the Elatec Vacuum Furnace, which is shown in Figure 3.3. Degassing was conducted before HIPing was applied and in-situ formation of TiB happened during the process. According to the literatures [11, 17, 18], degassing generally happens at 400°C and ends at around 700°C. So, the heating rate used from room temperature to 400°C was

$10^{o}C$/min and during $400^{o}C$ to $600^{o}C$, the heating rate should reduce to $2^{o}C$/min because most hydrogen will come out in this temperature range. The heating rate was changed to $5^{o}C$/min after $600^{o}C$ as the hydrogen keeps releasing out. The degassing process was set to stop at $800^{o}C$ in this project and then a trial sintering process was carried out to examine the sintering effect. $10^{o}C$/min was used after $800^{o}C$ and samples were kept for 2 hours in the vacuum furnace when sintering temperature, which is $1300^{o}C$, was reached. High purity argon went through the furnace during the degassing process in order to take all releasing hydrogen out of the facility and then the atmosphere was changed to vacuum, which was 10^{-4} torr, during the sintering process. After the sintering cycle, $5^{o}C$/min was used during the furnace cooling process from $1300^{o}C$ to room temperature. The designed process described above is shown graphically in Figure 3.4.

HIPing was conducted in AIP 6-30H Hot Isostatic Press machine at $1300^{o}C$ under high purity argon and the pressure was 100MPa. Samples were also put in the alumina crucible, surrounded by Ti metal swarf and kept in the facility for 2 hours. The facility is shown in Figure 3.5.

Figure 3.1 Turbular Mixer in ANSTO (by Tina Eddowes)

Figure 3.2 AIP CP360 Cold Isostatic Press in ANSTO (by Tina Eddowes)

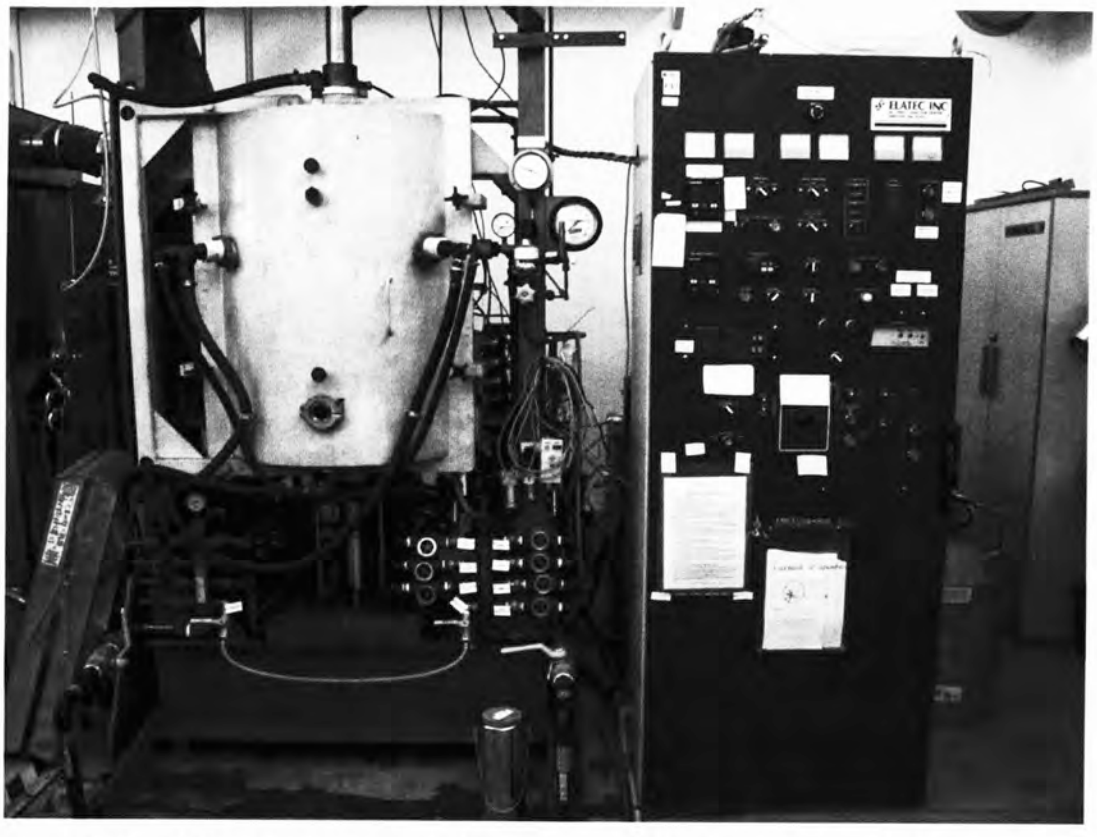


Figure 3.3 Elatec Vacuum Furnace in ANSTO (by Tina Eddowes)

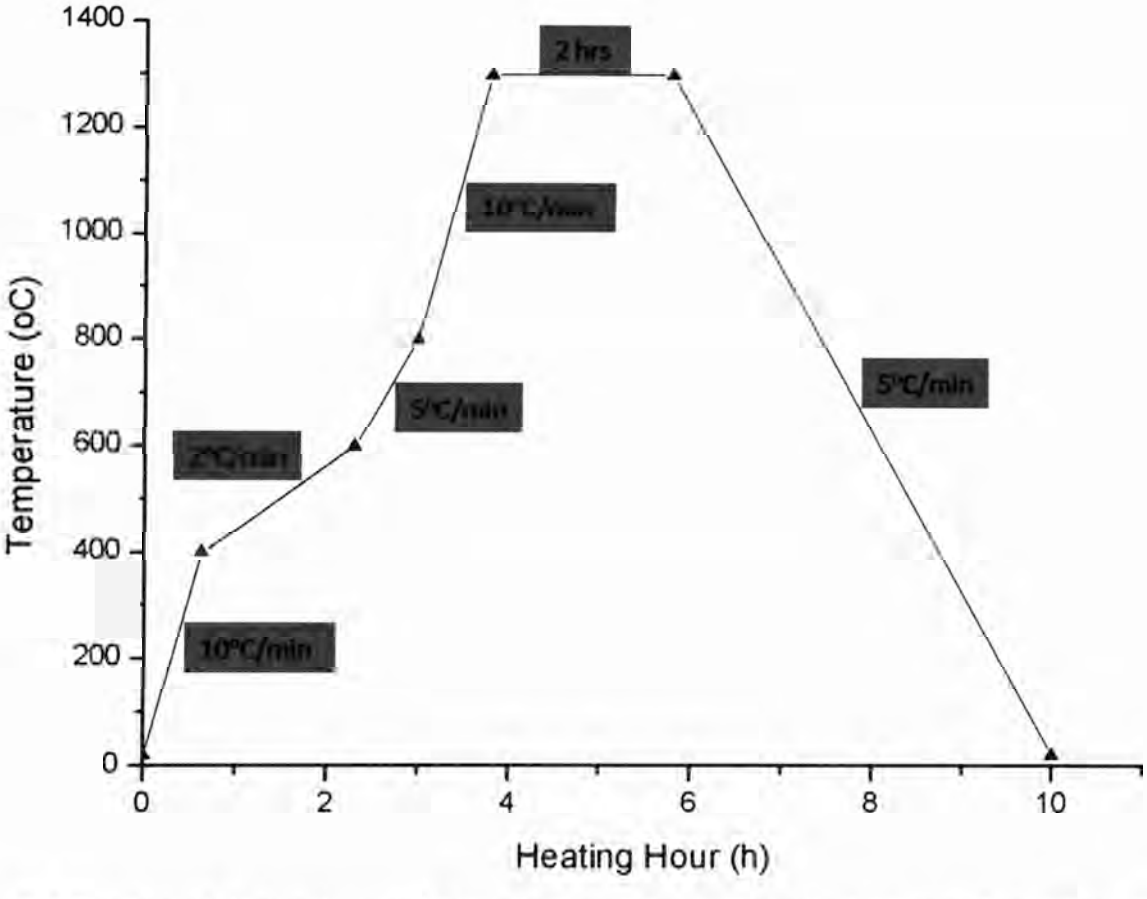


Figure 3.4 Designed degassing and sintering process of titanium composites samples with different amount of reinforcements in this project

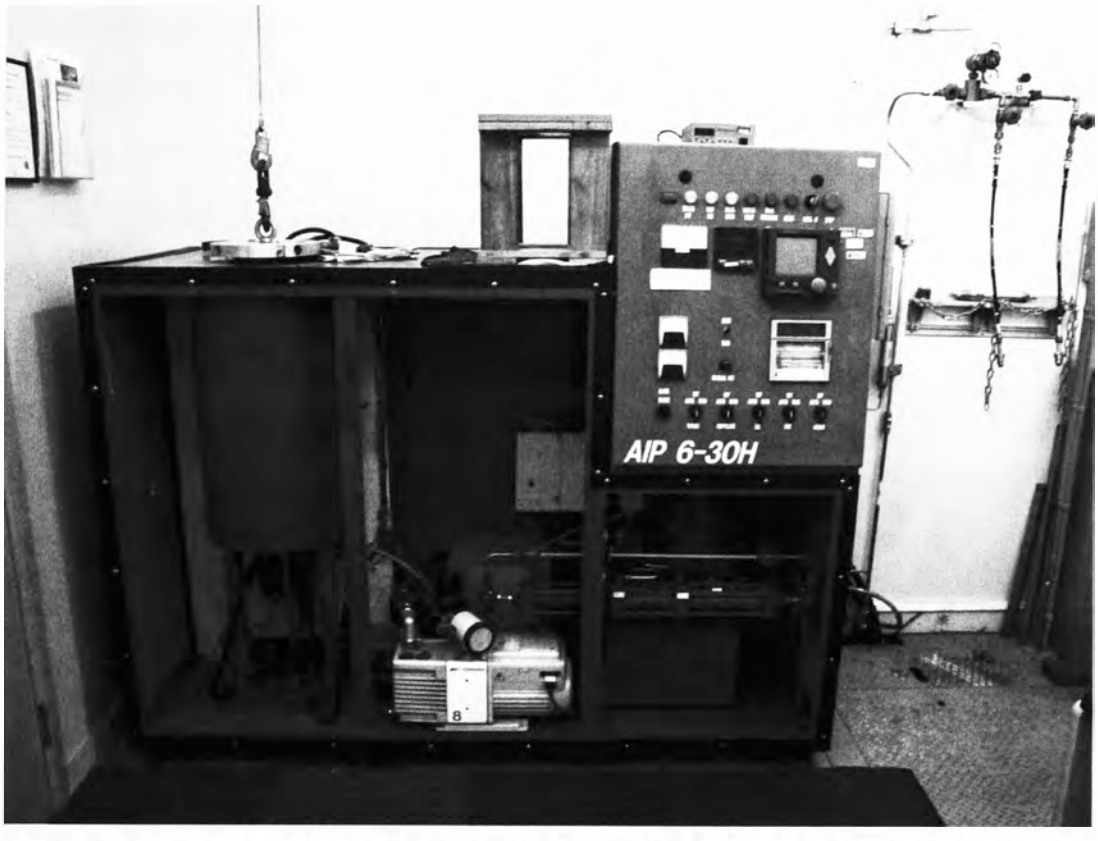


Figure 3.5 AIP 6-30H Hot Isostatic Press in ANSTO (by Tina Eddowes)

Properties of commercial titanium alloys composites exhaust valves and TMCs fabricated in this project were evaluated and compared. DSC, ICP (Chemical Analysis) and XRD examination, mechanical properties examination including the tensile test and hardness test, metallographic examination including optical microscopy and SEM on both kinds of products were carried out in UNSW.

Following paragraphs in this section are the description to all facilities used for examination in this project.

DSC (Differential Scanning Calorimetry) can be used to measure a number of characteristic properties of a sample. It is possible to observe fusion and crystallization events using this technique and DSC can also be used to study oxidation, as well as other chemical reactions. The DSC testing facility used in this project was SETARAM, which can also be used as DTA and TGA testing.

In ICP (Inductively Coupled Plasma) analysis, GBC Integra ICP AES instrument was used. ICP-AES (Inductively Coupled Plasma - Atomic Emission Spectrometer) uses ICP to produce excited atoms which emit electromagnetic radiation at a wavelength characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample.

All XRD experiments were carried out using Siemens D5000. Samples were exposed to a monochromatic Cu Kα radiation with a wavelength of 1.541838 Å. The voltage and the current were set as 30kV and 30mA respectively. The pattern obtained after XRD was compared to those from the literature (or JCPDS cards) to verify what the composition of the sample was. The software used to analyze XRD patterns was "X'pert high score plus".

Hardness and tension tests are general examination methods of mechanical properties. Facilities used in the testing were M-400-H1 LECO Hardness Testing Machine and Instron 1185 Tensile Testing Machine.

Optical microscopy (OM) and SEM are used to examine the microstructure of samples. Before OM testing, samples were etched by Kroll's reagent, which included 2mL hydrofluoric acid, 10mL nitric acid and 88mL distilled water. The optical microscopy in use was Nikon Epiphot 200. All SEM results were carried out using Hitachi S4500, S3400 and JEOL 840S in this project. Energy-dispersive spectrometry (EDS), which is equipped in it, is usually implemented to quantify the composition of a certain area of the sample surface.

Detailed results are stated in Chapter 4.

4 Results and Discussion

In the beginning of this chapter, properties of titanium matrix composite exhaust valves, which were from Toyota Motor Corporation, Japan, have been investigated in order to be compared with those of fabricated products in this project.

Secondly, examination results of the starting material, titanium hydride powder which was from AG Materials Inc., Taiwan, and the reinforcement, titanium diboride powder which was from DanDong Chemical Engineering Institute Co. Ltd, China, will be described.

Composition evaluation and properties examination of TMCs products manufactured in ANSTO will be stated in the last part of the chapter. All percentage in this thesis represents the weight percent.

4.1 Titanium Matrix Composites Exhaust Valves

The commercial exhaust valves are made of titanium alloys matrix composites with titanium boride reinforcement [3]. In their processing, titanium hydride powder and titanium diboride powder were used as the same purpose described in this thesis. For the strengthening alloying elements, a master-alloy powder of Al-25Sn-25Zr-6Nb-6Mo-1.2Si was prepared by an inert-gas atomization method (All numbers represent the weight percent of each element) [3]. So, the matrix of valves is the near alpha alloys, which have higher tensile strength than fully alpha alloys in room temperature and show the greatest creep resistance among all titanium alloys at above 400°C. They can also be strengthened by heat treatment [13].

In this part, different testing results are listed, which are ICP-AES, XRD, OM examination, hardness, tensile testing and SEM testing for the fracture surface. According to the first two testing methods, the compositions of the commercial exhaust valves are acquired. Mechanical properties are derived from tensile and hardness testing and microstructures of the fracture surface after tension testing are obtained from the SEM.

4.1.1 ICP Result

Analyte	Samples Identification & Results (wt%)
Titanium (Ti)	88.5
Boron (B)	0.92
Aluminium (Al)	4.84
Zirconium (Zr)	3.6
Niobium (Nb)	0.9
Molybdenum (Mo)	0.89
Silicon (Si)	<0.5

Table 4.1 Weight percent of each element in the commercial exhaust valves

Table 4.1 shows the amount of different elements exist in the commercial exhaust valves. In the literature, the matrix material used in commercial exhaust valves is the titanium alloy, which is near alpha alloy and the composition can be concluded as Ti-6Al-4Sn-4Zr-1Nb-1Mo-0.2Si-0.3O [3]. So, ICP results match well with the composition reported. Tin and oxygen can not be detected by this kind of chemical analysis.

The calculation result of the weight percent of TiB_2 added into the matrix can be obtained by mass-mol equation if the assumption that all TiB_2 has already transformed into TiB is made and the value acquired is approximately 3%.

4.1.2 XRD Spectrum

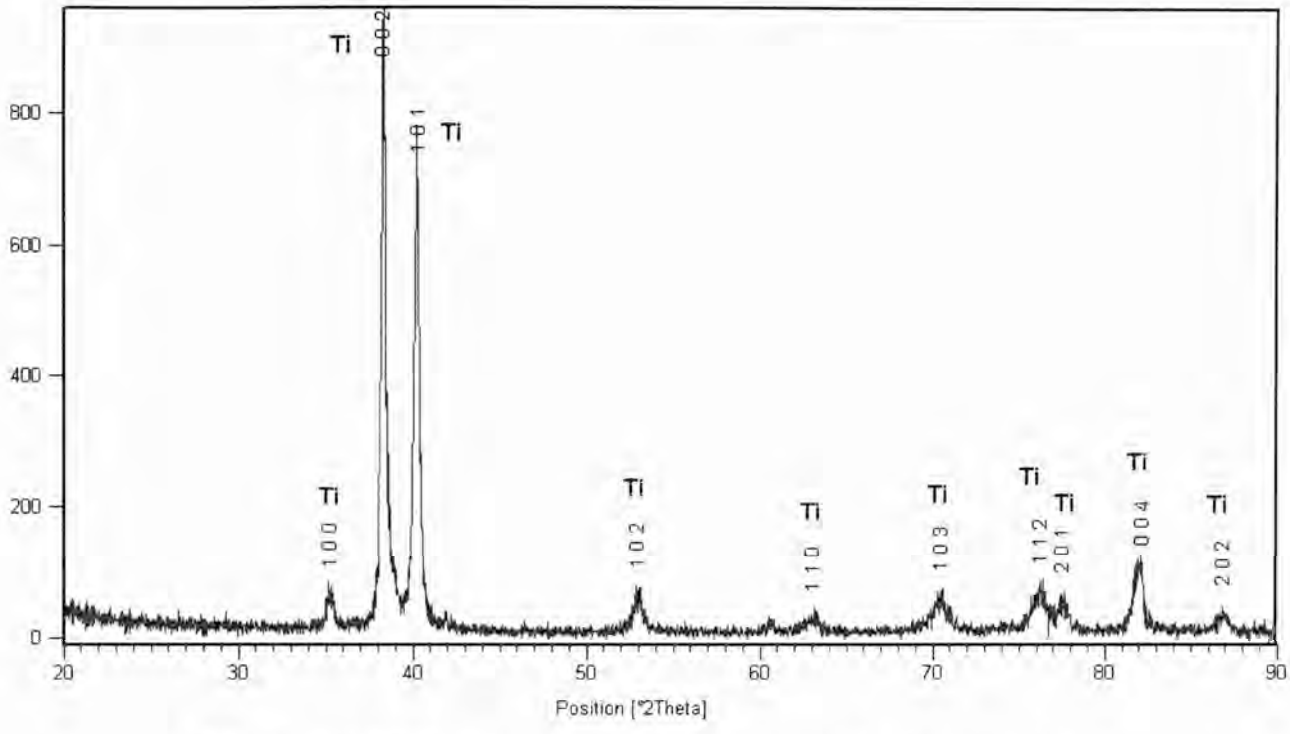
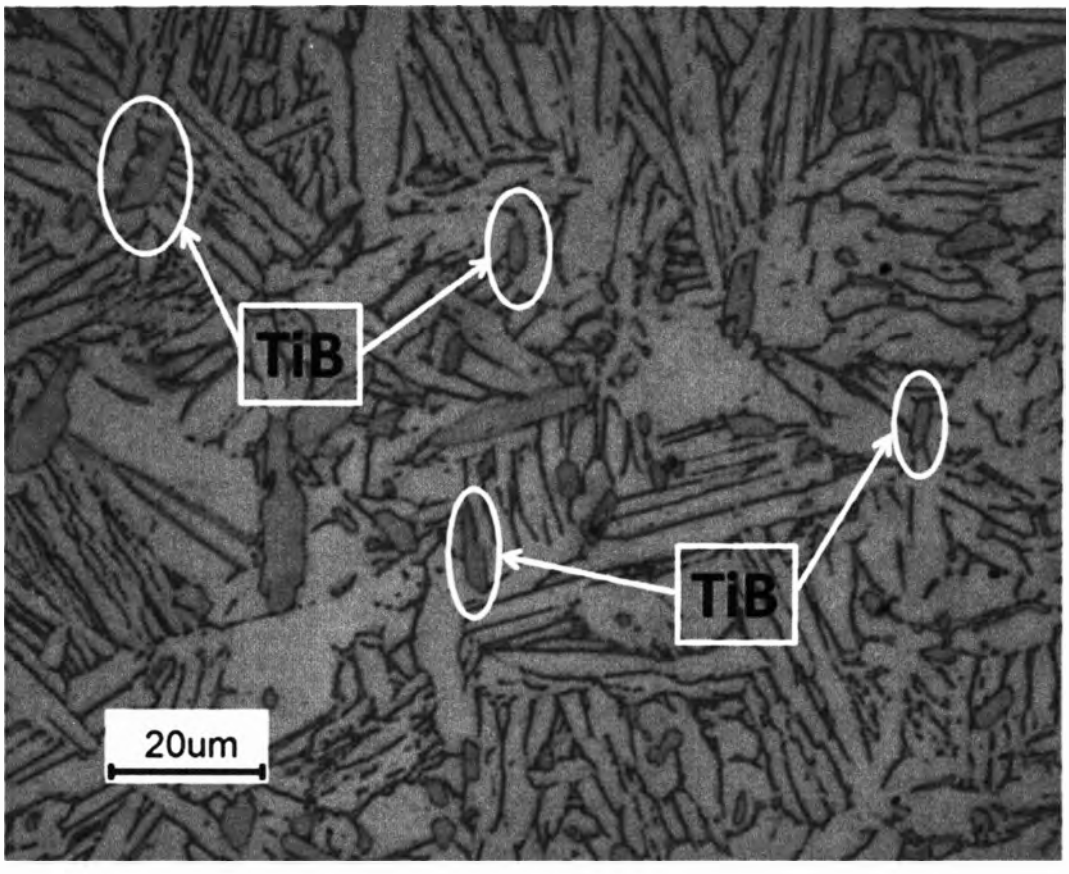


Figure 4.1 XRD Spectrum of the commercial exhaust valves

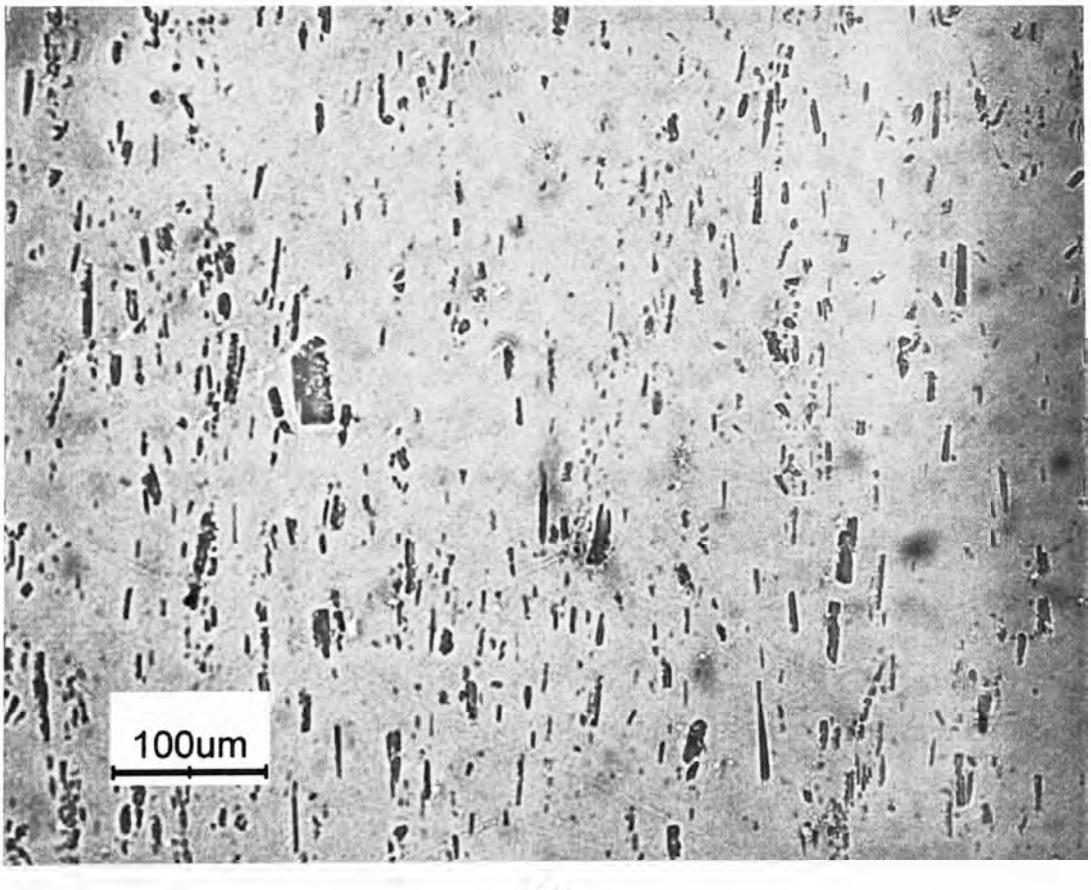
The XRD pattern shown in Figure 4.1 indicates that nearly all composition of the commercial exhaust valves is titanium. With 3% addition of reinforcement, the TiB formation is hard to be detected. Alloys elements are also inconspicuous on the pattern.

4.1.3 Optical Microscopy Results

Figure 4.2 shows the OM images of cross-section and longitudinal directions of an exhaust valve. The transverse direction was etched by Kroll's reagent. Widmastatten structure is evident in Figure 4.2a and TiB reinforcements, which are circled on the image, distribute evenly along the grains. In Figure 4.2b, most of the reinforcements align in the same direction, which is the extruding direction. It can concluded here that the length of the TiB whiskers is about 70~80 μm and the width of them is about 10~20 μm.



(a)



(b)

Figure 4.2 Optical microscopy images of commercial exhaust valves: (a) Transverse Direction (b) Longitudinal Direction

4.1.4 Hardness Results

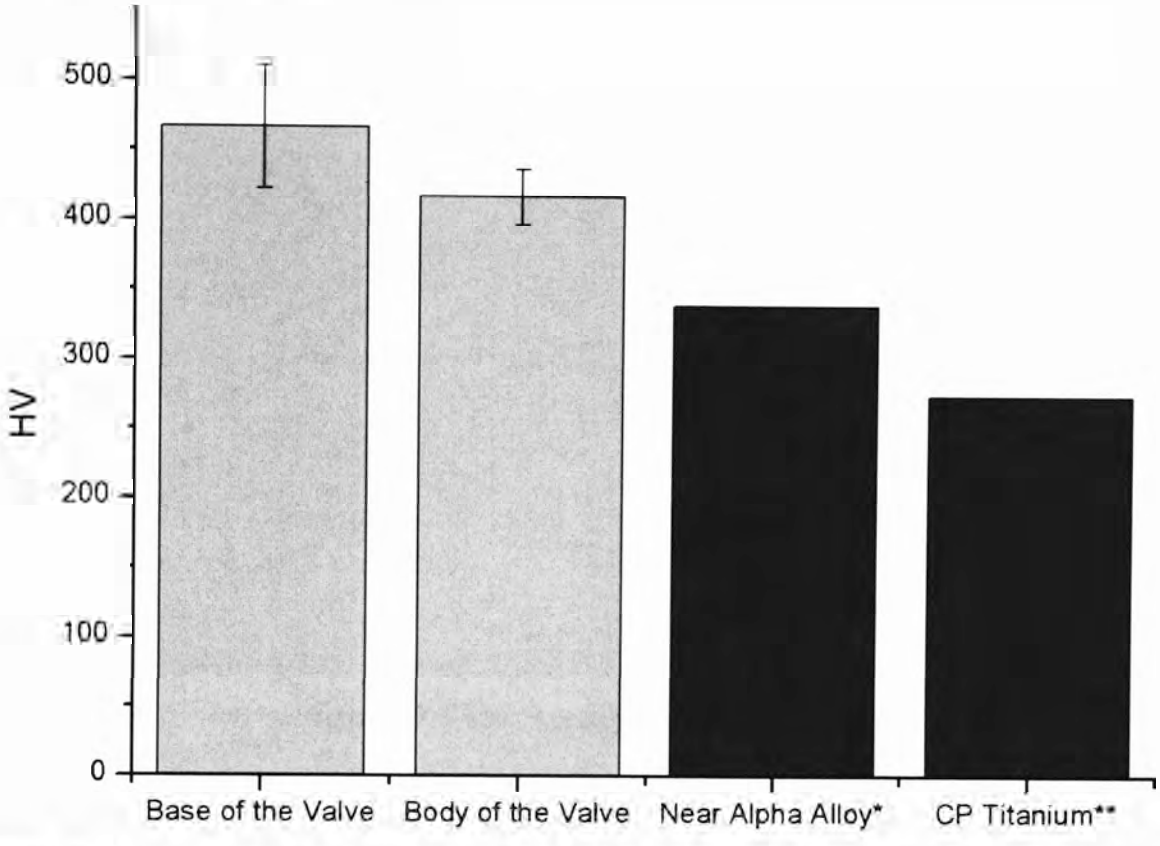


Figure 4.3 Comparison of Vickers hardness between commercial exhaust valves, near alpha alloy and CP titanium (* Ti-8Al-1Mo-1V, Annealed ** 99.0wt% Ti, Grade 4, Annealed) [30]

Figure 4.3 shows the comparison of Vickers hardness between valves, near alpha alloys and CP titanium. It is apparently that the exhaust valves are much harder than matrix materials and CP titanium. Since the base of the valve is forged, a work hardening effect can result in the increasing hardness value compared with that of the valve body. The scattering of hardness value of the valve base is about 40 and the one of the valve body is about 20. This may be attributed to randomly distributed reinforcements in the base, which is not subject to extruding processing. The chance to hit the reinforcements on the surface of the base increases as that on the surface of the body.

4.1.5 Tensile Sample and Results

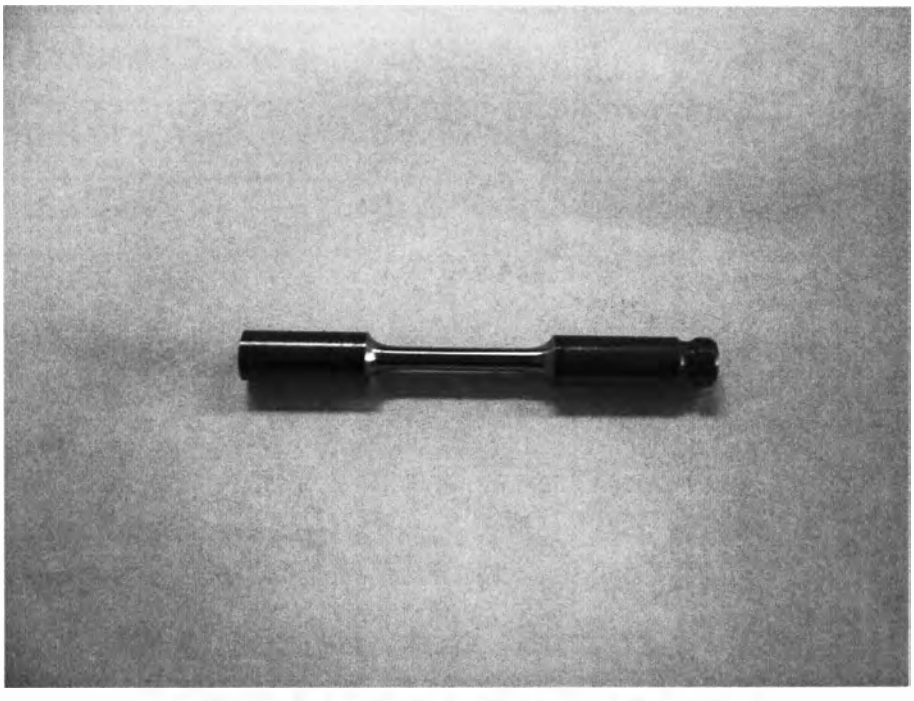


Figure 4.4 The machined tensile sample

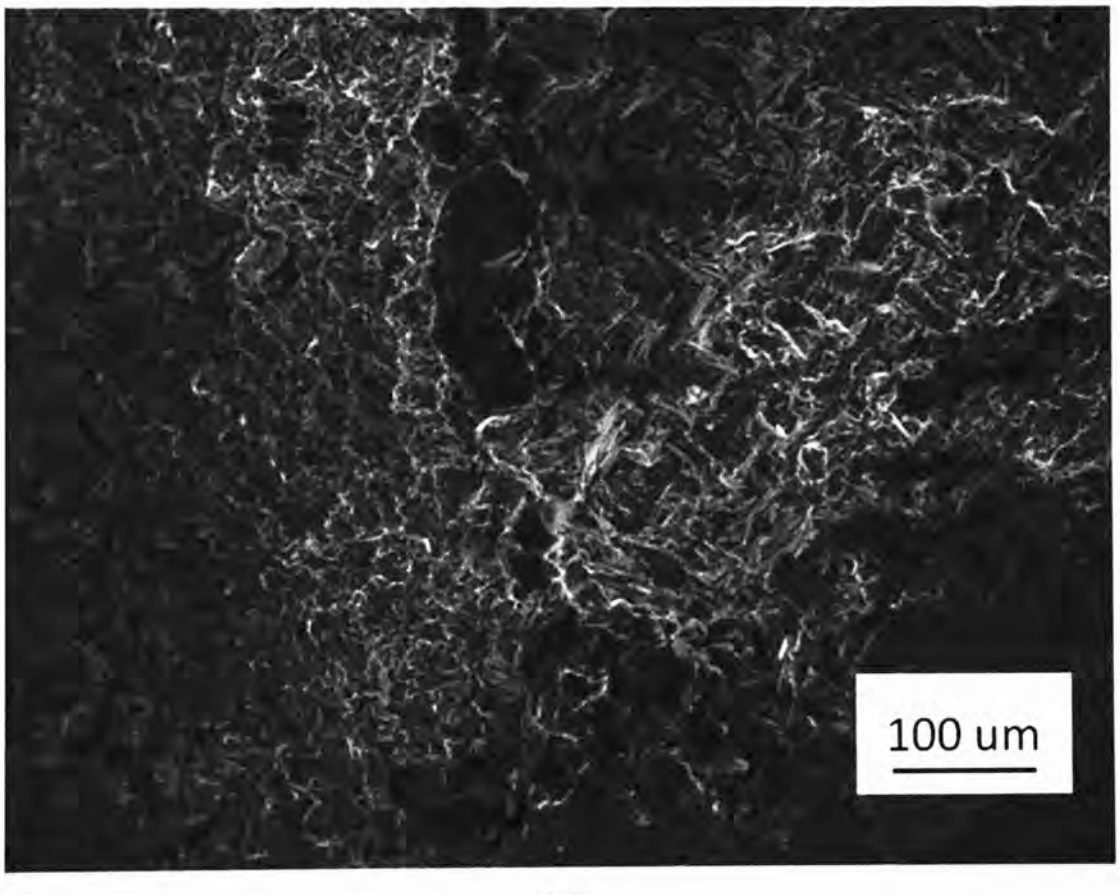
The exhaust valves were machined to carry out the tensile testing. Figure 4.4 shows the machined sample, with a center part diameter of 2.5mm and a gage length of 14mm, which is about five times of the center part diameter, meeting the standard for tensile testing samples.

During the testing, 10kN load cell is applied. Samples broke near the center part, with the maximum load of 5.95kN, original area of 4.9mm^2 and length change of 0.4mm. Tensile results are shown in Table 4.2. According to the results, the tensile strength of the commercial valves is about 300MPa higher than the matrix materials. The Young's modulus is about 30GPa higher than near alpha alloys and CP titanium, which is abnormal due to the rule of mixture. The elongation of TMCs, which represents the ductility, is usually much lower than titanium alloys and CP titanium.

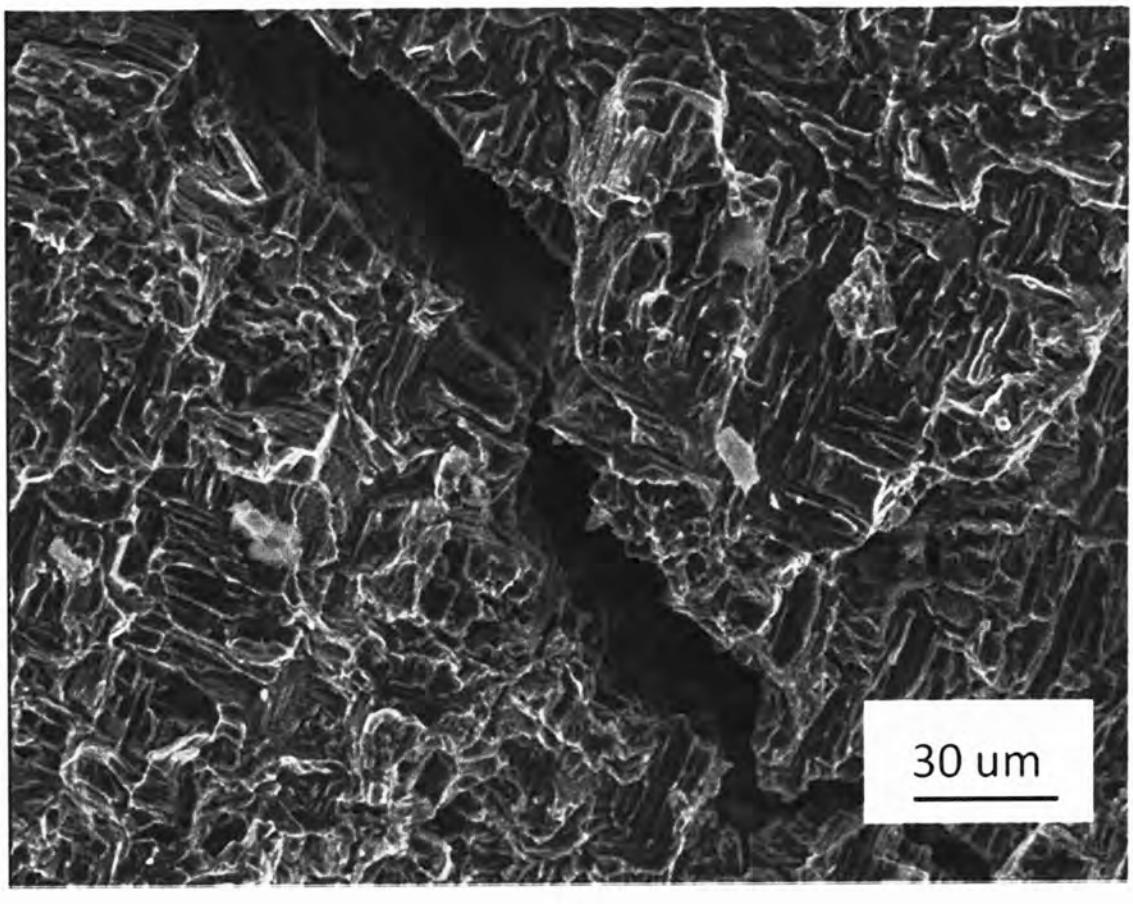
	Tensile Strength	Young's Modulus	Elongation
Commercial Exhaust Valve	1214MPa	140GPa	3%
Ti-6Al-2Sn-4Zr-2Mo	900~980MPa	113.8GPa	15%
CP Titanium	240~370MPa	105~120GPa	20%~30%

Table 4.2 Comparison of mechanical properties between commercial valves, a typical near alpha alloy and CP titanium [30]

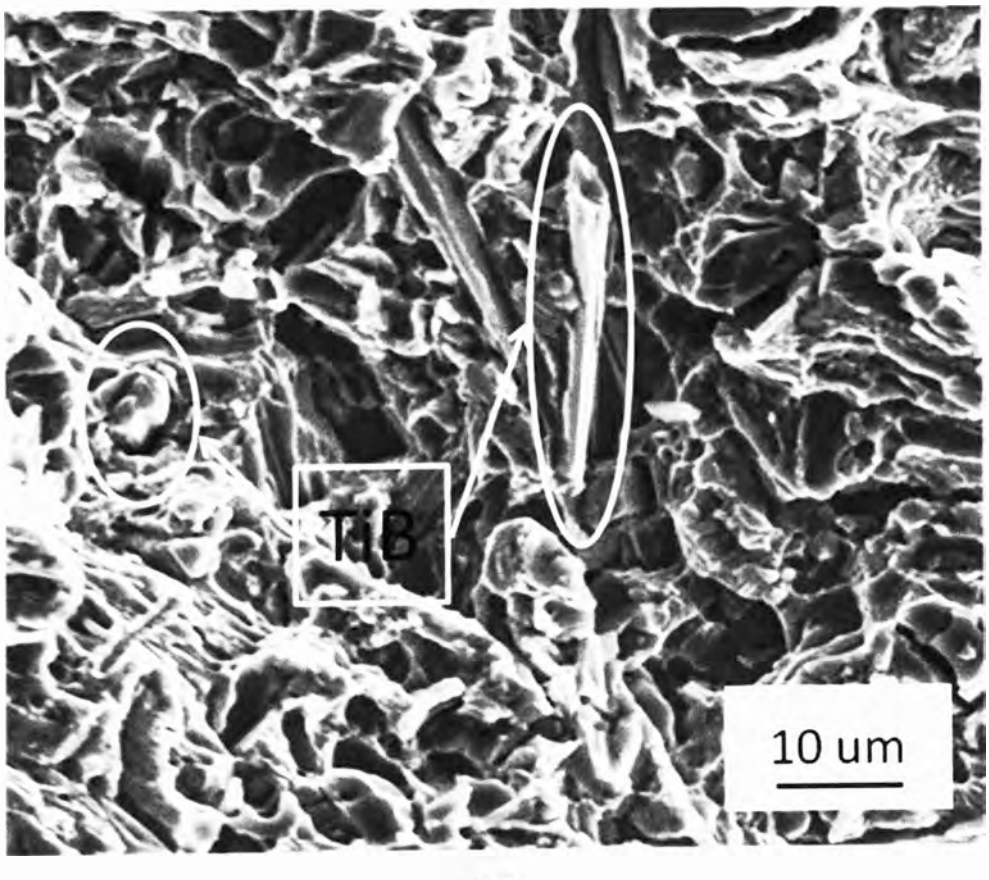
4.1.6 SEM Results of the Fracture Surface



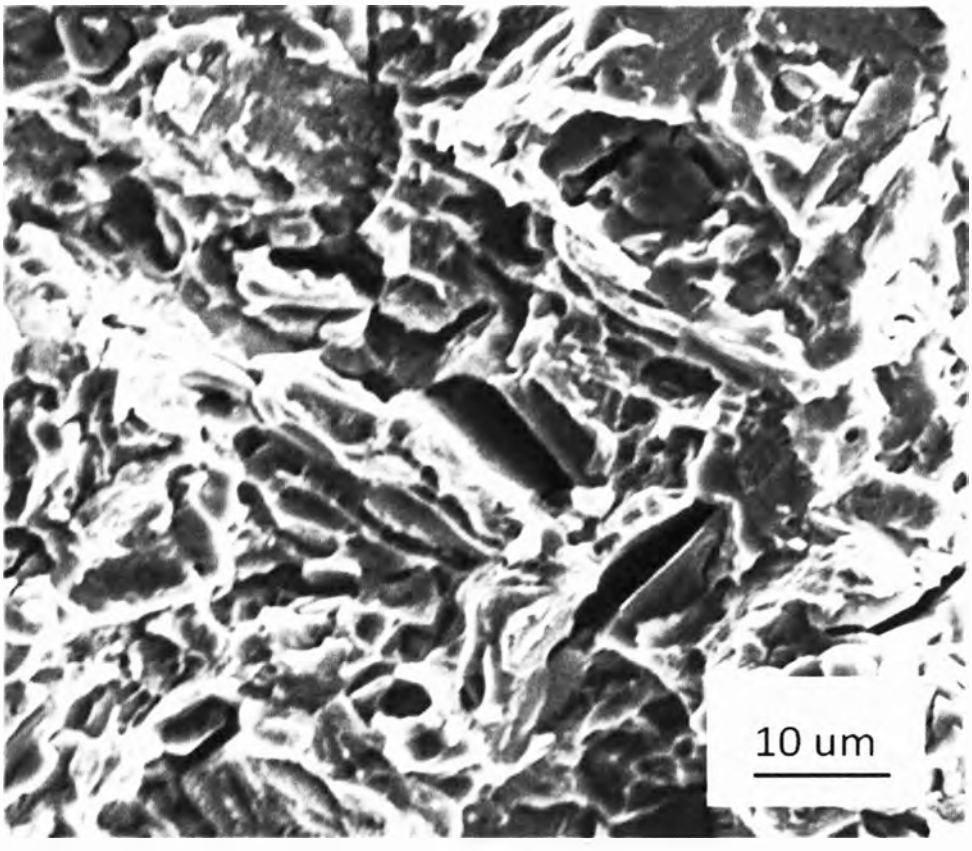
(a)



(b)



(c)



(d)

Figure 4.5 SEM images of the cross section of the exhaust valves: (a) Cross-section shows the Widmanstatten structures (b) Cracks cuts through the titanium grains (c) Broken reinforcement and decohesion effect are detected (d) Voids left in the matrix because of the pulling out of TiB

The fracture surface after tensile testing was examined under SEM. From Figure 4.5a and 4.5b, the existence of Widmanstatten structures is evident on the surface. This kind of structure has been discussed in part C, Chapter 2.2.2. The samples are brittle since cracks cut across the matrix grains in Figure 4.5b. Broken reinforcement and decohesion between the reinforcement and matrix are detected in Figure 4.5c. If the cohesion between the reinforcement and matrix is good, then most of the load will apply on the TiB reinforcement, resulting in the broken effect. If the decohesion effect exists as well, then the TiB reinforcement is easily to be pulled out, with voids shown in Figure 4.5d. The mechanism to explain the contradiction needs to be found out in the future research, such as wear testing.

4.2 Titanium Hydride Powder

4.2.1 XRD Spectrum

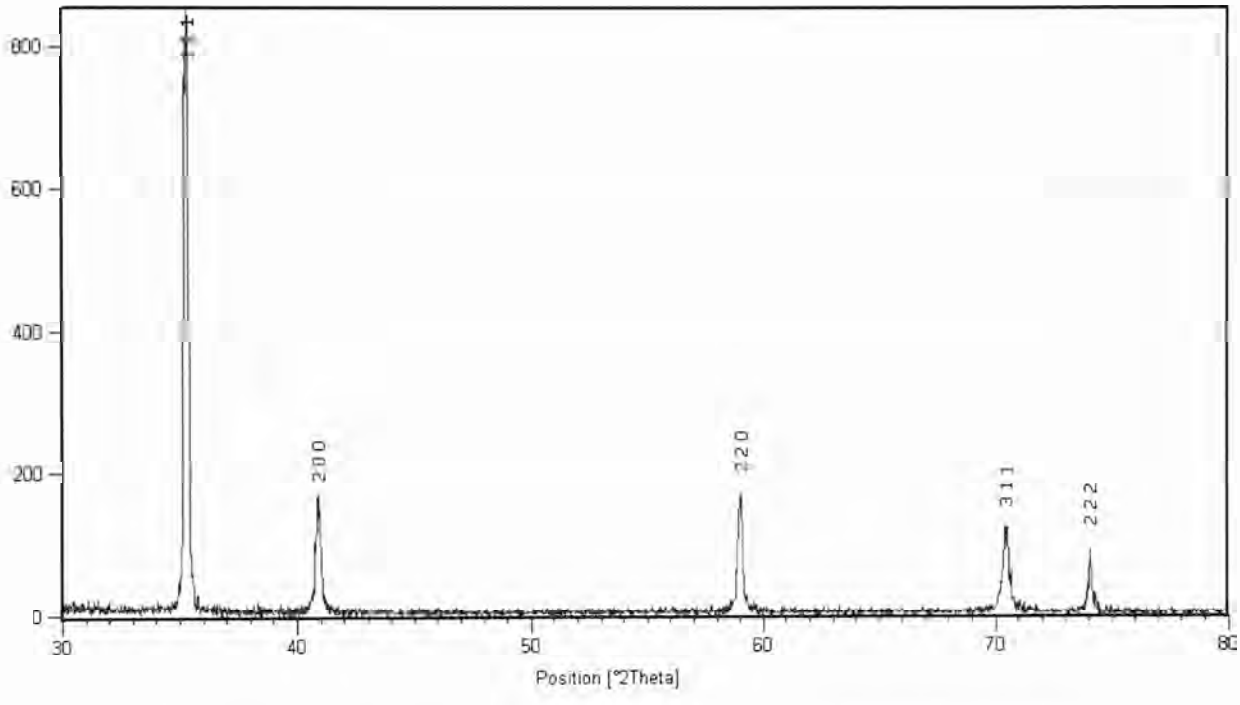


Figure 4.6 The XRD pattern of the titanium hydride powder

Comparing the results in Figure 4.6 with the data in the JCPDS card number 25-0982, the starting material powder is exactly the same with the substance in the card. So it can be concluded that the chemical formula of the powder is $TiH_{1.924}$, and it belongs to the cubic crystal system.

4.2.2 SEM and EDS Results

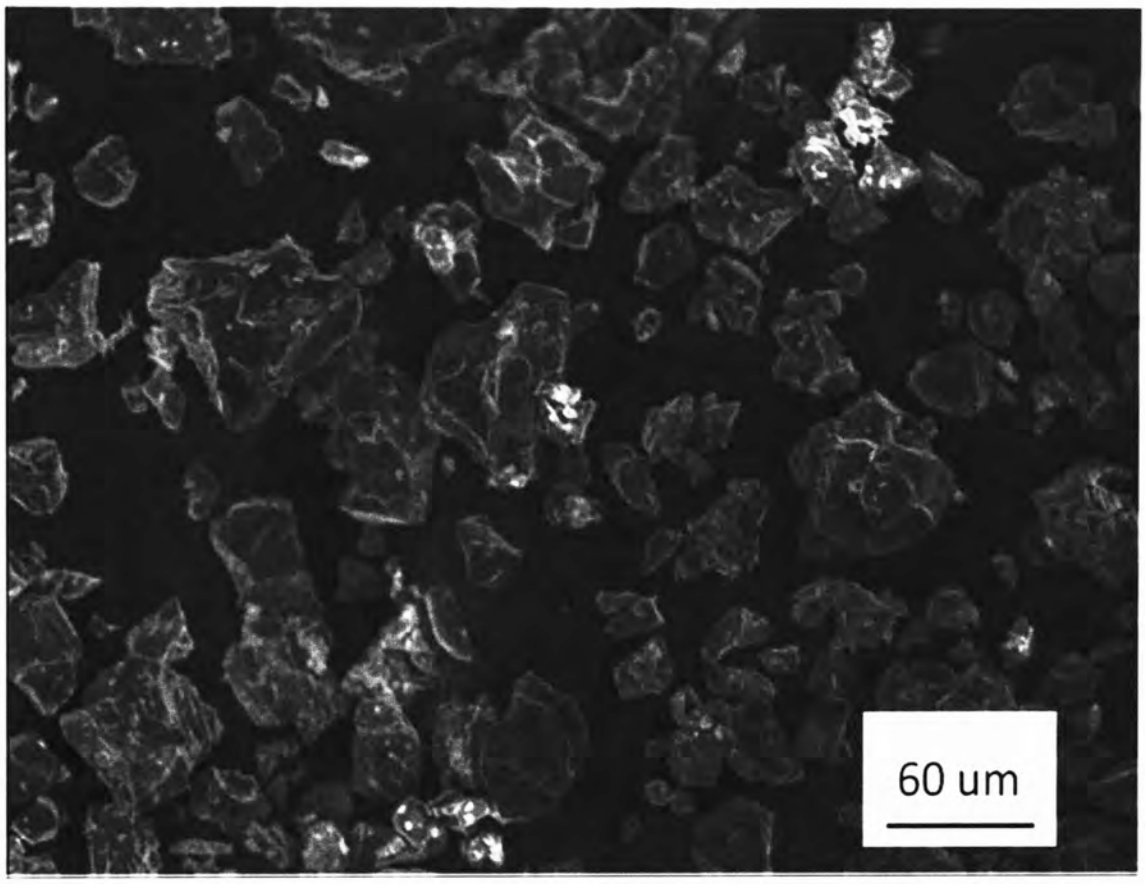


Figure 4.7 The SEM image of the titanium hydride powder and particles

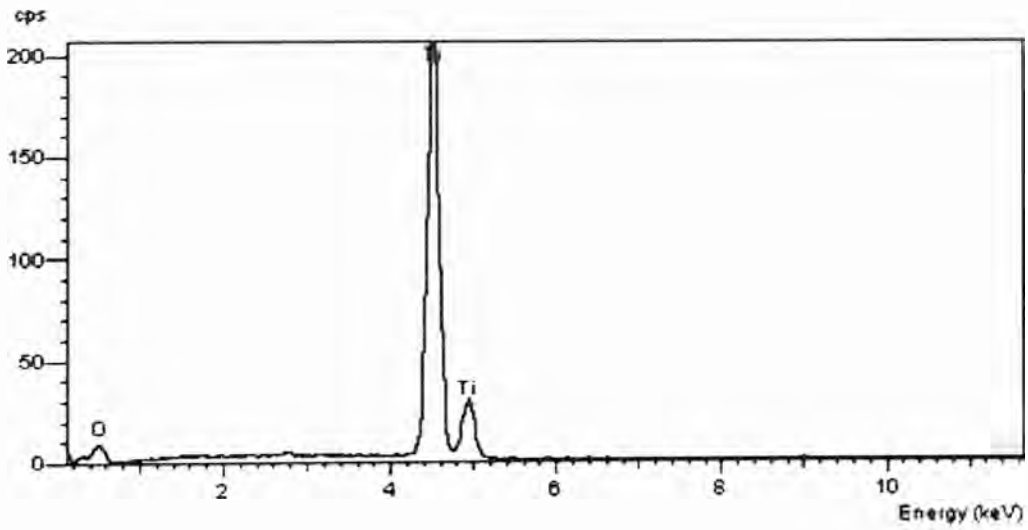


Figure 4.8 The EDS pattern of Figure 4.7

Through Figure 4.7, it can be observed that the size of the particle is mainly around 10~20 μm and some large particles are also found. Particles are of tetragonal shapes, verifying the comment, which shows that the powder will transform to tetragonal phase below 25°C in the JCPDS card number 25-0982.

The EDS pattern in Figure 4.8 shows that the substance mainly consists of titanium. Hydrogen can not be detected through the EDS. The existence of oxygen is also observed because of the oxidation of the powder in the air. The purity of the powder is very high according to the pattern.

4.2.3 DSC Result

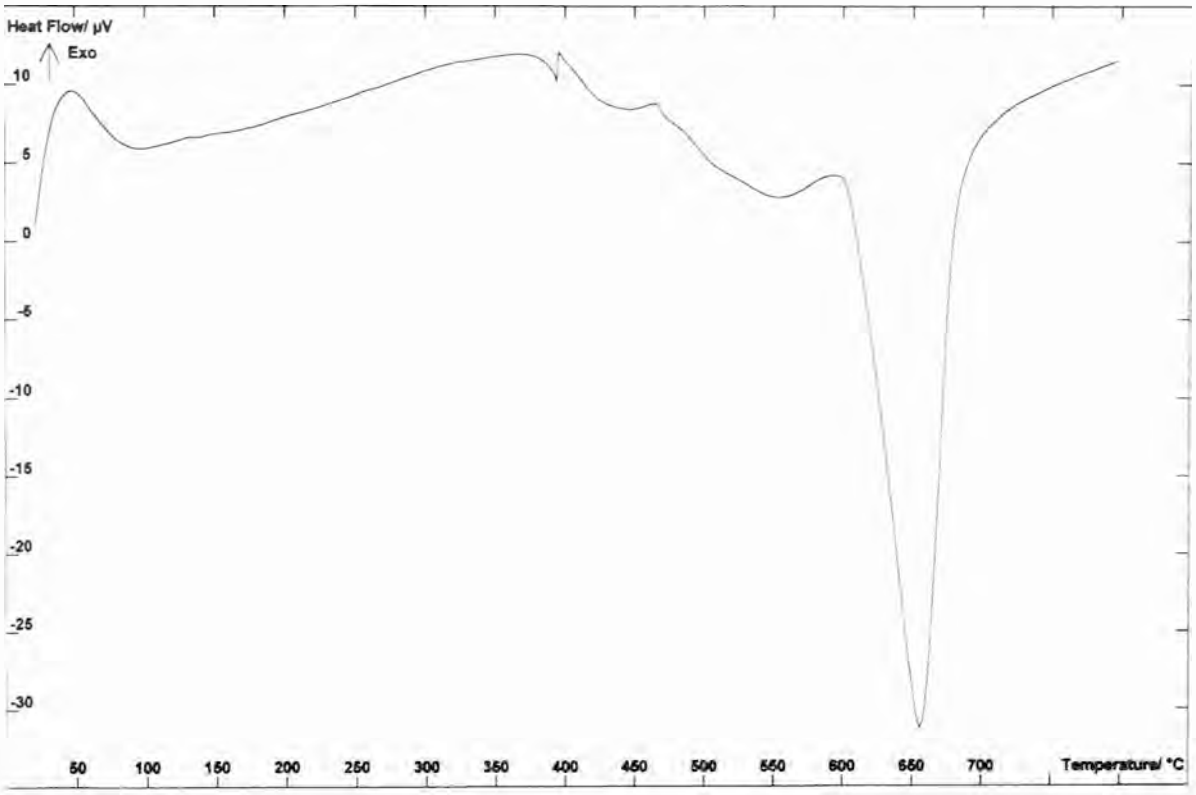


Figure 4.9 The DSC pattern of titanium hydride powders

DSC was carried out to verify the dehydrogenation process of titanium hydride powders. In Figure 4.9, endothermic process, which represents the reaction of dehydrogenation, takes place after about 400°C and continues until an endothermic peak is found at around 650°C. Exothermic reaction, which represents the heat generation during the dissociation of TiH_2, also happens during the temperature range but is suppressed by the endothermic process. After 650°C, exothermic process becomes the main trend as nearly all titanium hydride powders have finished dissociation. As a conclusion, dehydrogenation process of titanium hydride powders mainly happens between 400°C and 650°C, and stops at about 750°C according to the DSC pattern.

DSC testing on titanium hydride powders with titanium diboride powders was also carried out and it formed the same pattern as the one shown in Figure 4.9. So, the boron phase will not affect the dehydrogenation process and the TiB formation reaction begins after 700°C.

4.3 Titanium Diboride Powder

4.3.1 XRD Spectrum

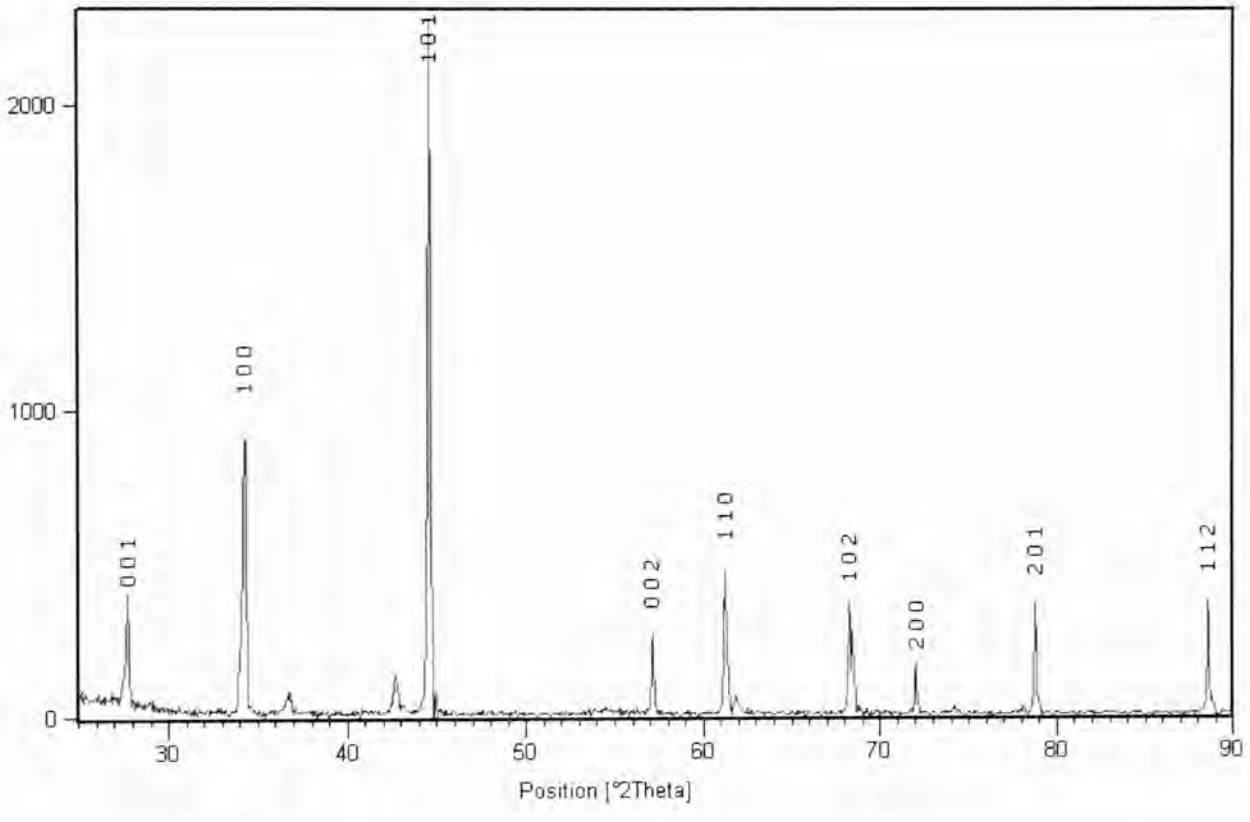


Figure 4.10 The XRD pattern of the titanium diboride powder

Comparing the values in Figure 4.10 with the data in the JCPDS card, it can be concluded that the substance is titanium diboride, and it belongs to the hexagonal crystal system. Some impurities are found according to unmarked peaks, with the amount of about 5% reported by the manufacturing company.

4.3.2 SEM and EDS Results

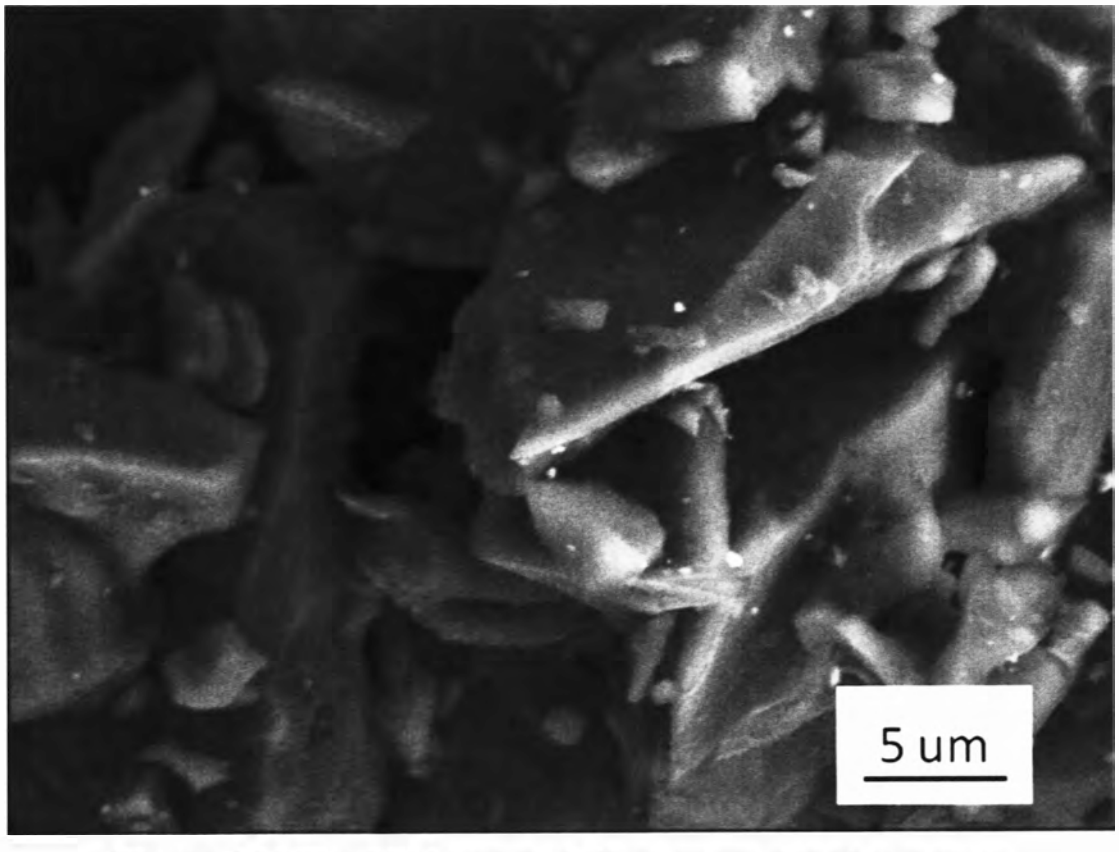


Figure 4.11 The SEM image of the titanium diboride powder

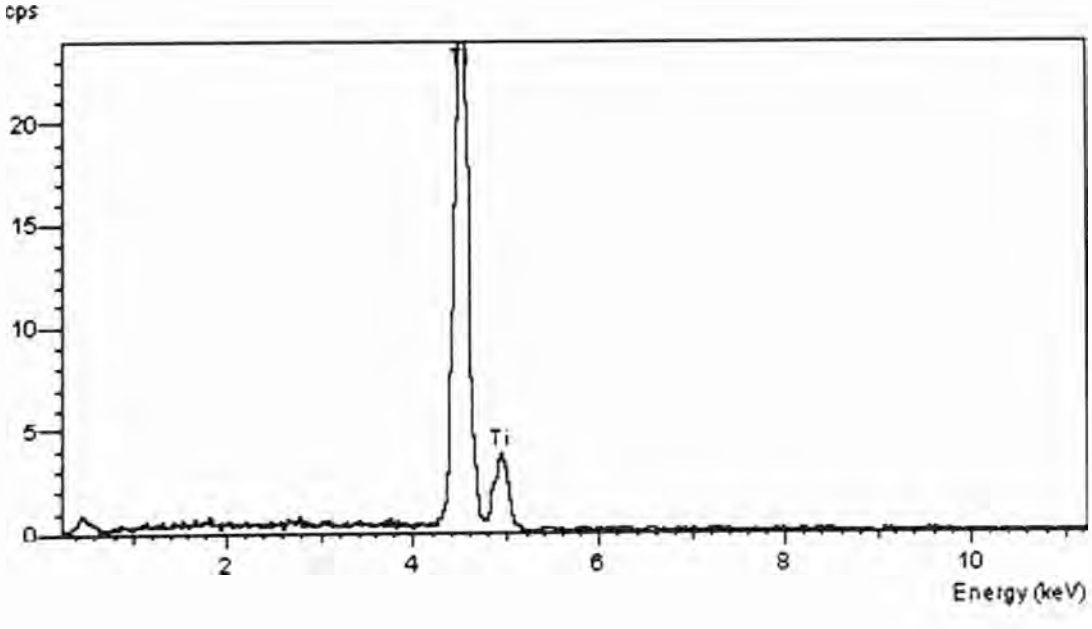


Figure 4.12 The EDS pattern of Figure 4.11

From Figure 4.11, it can be observed that sizes of titanium diboride particles vary from sub-micron to tens of micron. Most of particles are in the range from 2 to 20 μm. Particles which are larger than 50 μm and smaller than sub-micron meters are also detected. Size-distribution examination needs to be done to acquire detailed sizes of these particles.

The EDS pattern in Figure 4.12 shows that the powder mainly consists of titanium. Boron can not be detected through the EDS.

4.4 Titanium Matrix Composites Reinforced with Sub-micron TiB Particulates

4.4.1 Appearance and Hardness of the Trial Titanium Sample

4.4.1.1 Appearance

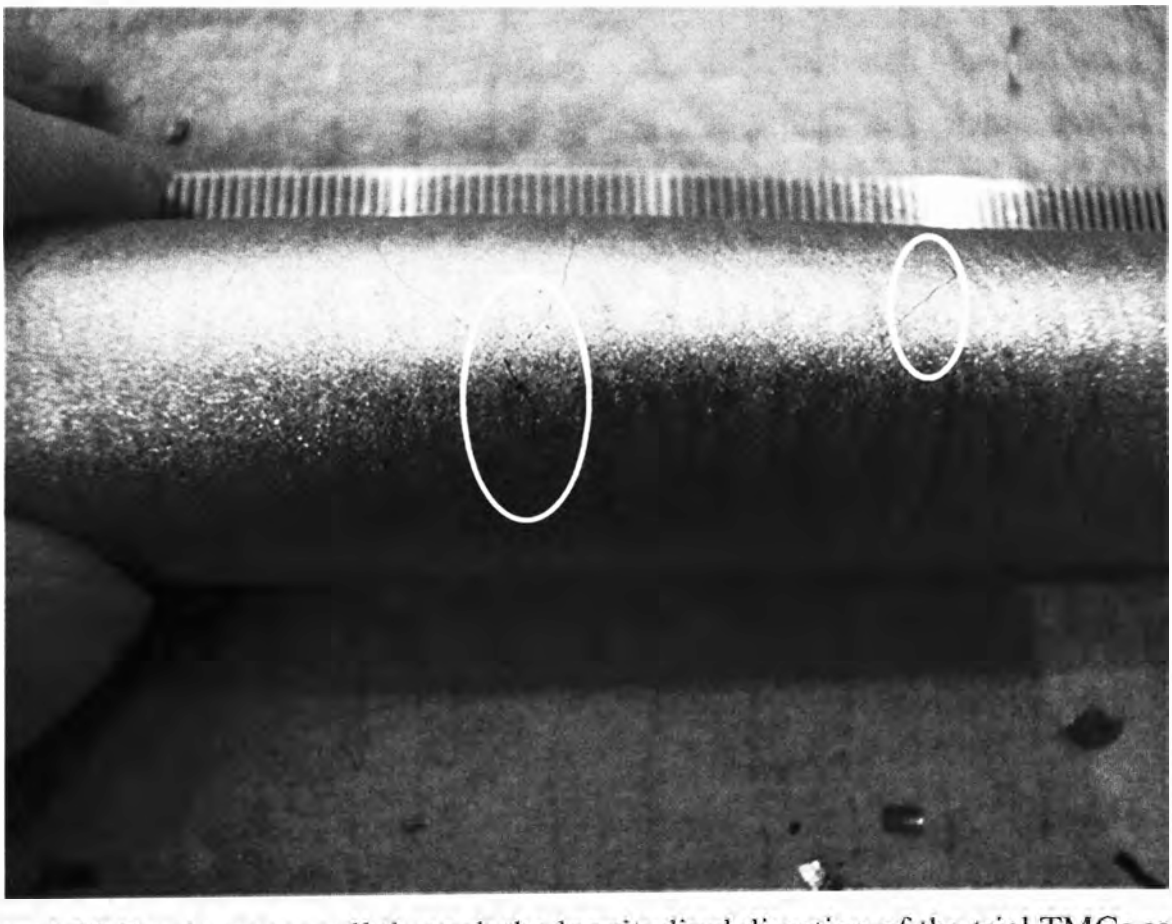


Figure 4.13 Cracks appear all through the longitudinal direction of the trial TMCs sample (by Tina Eddowes).

One trial titanium sample without any reinforcement of this project was manufactured following the process described in Chapter 3.2. Cracks were found all through the longitudinal direction of the sample after sintering, as shown in Figure 4.13. After cutting

on the cross-section, cracks were found running across the sample. The density of the sample after sintering has reached 96.4% of the theoretical density. One part of the sample without apparent cracks was cut off to finish the HIPing process. The appearance of the HIPed sample is shown in Figure 4.14 and the density of it has reached nearly 100% of theoretical density.

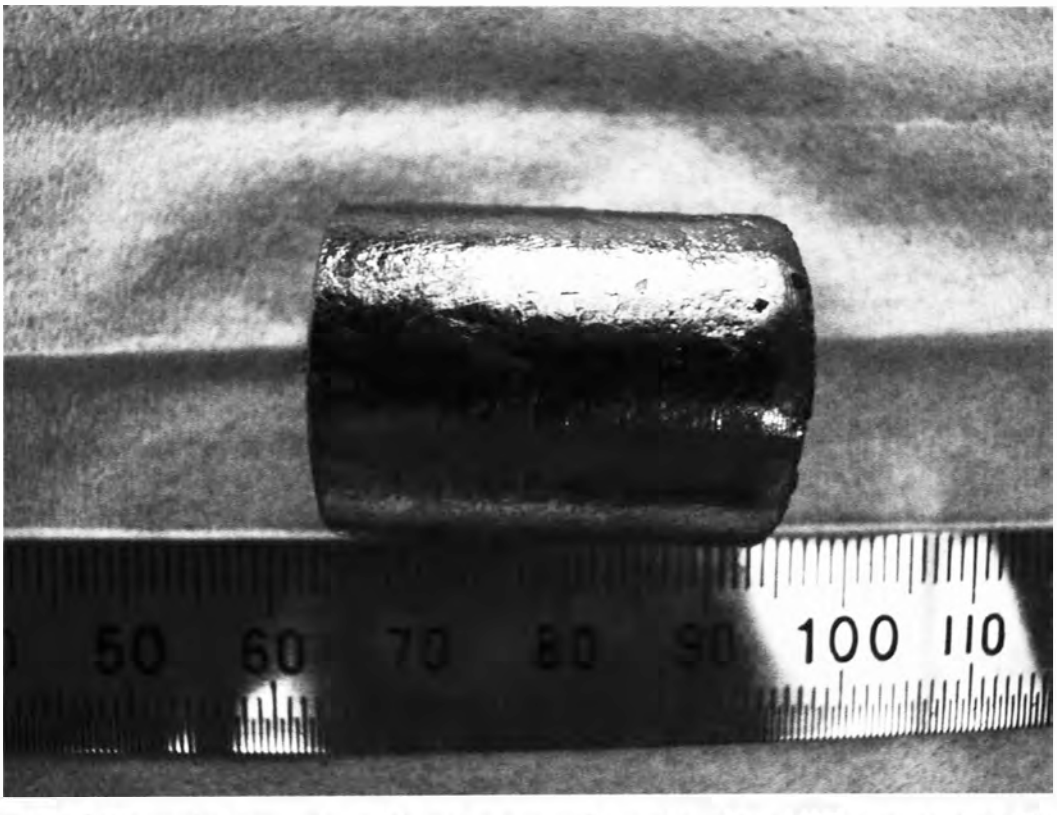


Figure 4.14 The trial sample without apparent cracks after HIP processing (by Tina Eddowes)

4.4.1.2 Microstructure and Hardness Evaluation of HIPed Sample

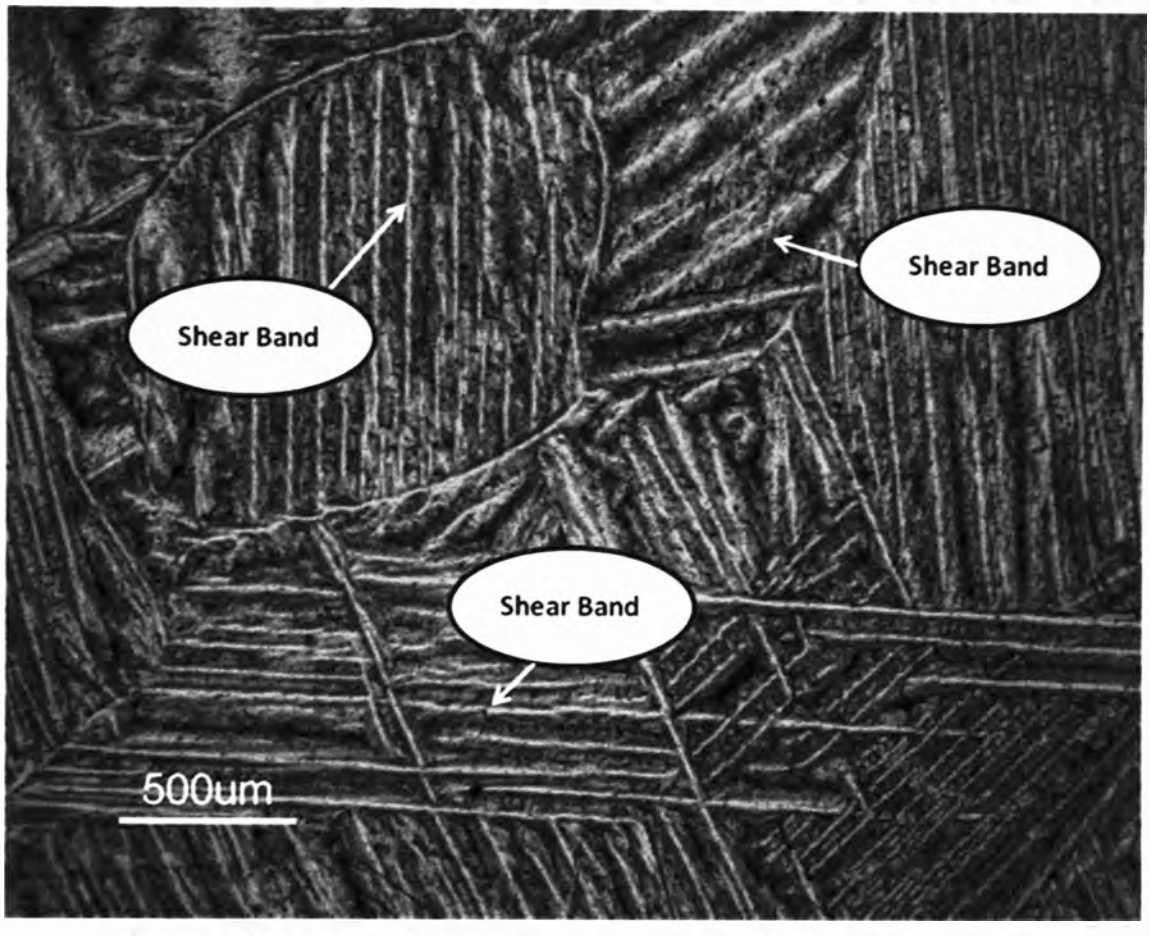


Figure 4.15 Optical microscopy images of HIPed trial sample

The HIPed sample was etched by Kroll's reagent on the cross-section and examined under the optical microscope. Figures 4.15 indicates the microstructure of the pure titanium sample, showing the shear bands, which are caused by high temperature and high pressure, aligned in different directions in the material. Similar structures were reported by Y. B. Gu's work [31], which mainly focused on the dynamic behavior of HIPed Ti-6Al-4V and the sample was subject to the Hopkinson bar test.

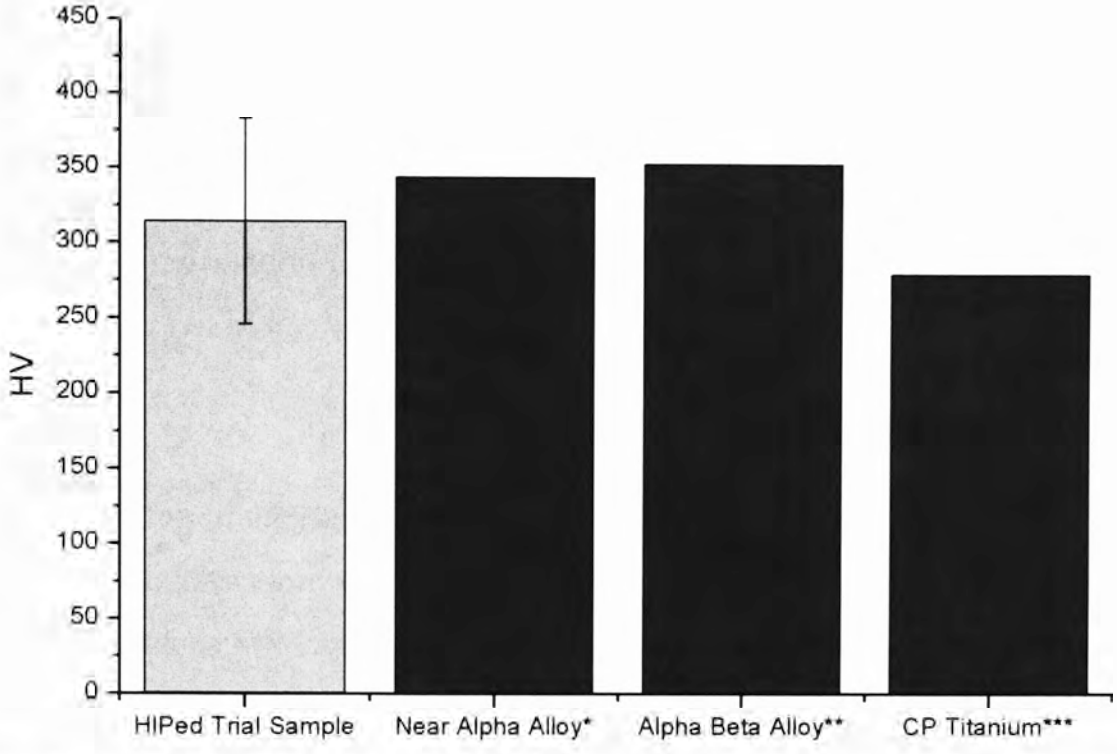


Figure 4.16 Comparison of Vickers hardness between HIPed trial sample, near alpha alloy, alpha beta alloy and CP titanium

(* Ti-8Al-1Mo-1V, Annealed ** Ti-6Al-4V, Annealed *** 99.0wt% Ti, Grade 4, Annealed) [30]

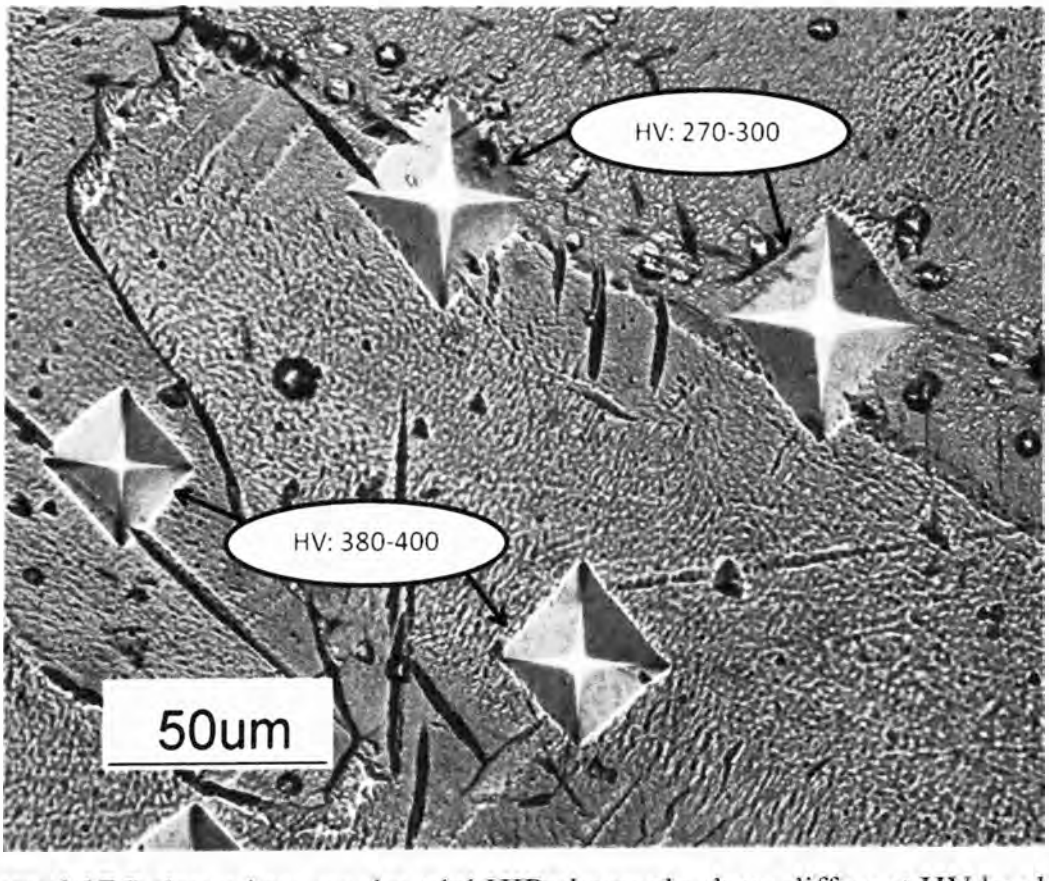


Figure 4.17 Indentations on the trial HIPed sample show different HV hardness

The comparison of the hardness between the HIPed sample, near alpha alloy, alpha beta alloy and CP titanium is shown in Figure 4.16. It can be obtained that the hardness of HIPed pure titanium sample is nearly the same as that of titanium alloys. The strengthening mechanism is still not clear and needs to be found out in the future study. In Figure 4.17, different size of indentation has shown that the HIPed sample is much harder in the grain than on the grain boundary, which is unusual as the grain boundary should be harder than the inner grain.

The large scattering of the hardness value of the trial HIPed sample was believed to be due to the plastic deformation of the material during hipping, but future microstructure examinations, such as SEM and TEM need to be done to find out the detailed mechanism.

4.4.2 Properties of Fabricated TMCs Samples with Different Amount of Reinforcements

Four kinds of samples were fabricated following the process described in Chapter 3.2. Cracks appeared on the surfaces of all samples. HIP processing didn't apply on any sample with cracks and the density of each sample after sintering has reached about 96% of the theoretical density.

In this section, chemical analysis and XRD were carried out to examine the real composition of each sample. OM and SEM images indicated the microstructures of samples with different amount of reinforcements. For mechanical properties examination, tensile testing can not be done due to cracks existence and only hardness results are shown in this section.

4.4.2.1 ICP Results

Analyte	Samples Identification & Results (wt%)			
	0%	1%	3%	5%
Titanium (Ti)	99.4	98.5	97.8	96.9
Aluminium (Al)	0.32	0.66	0.72	0.87
Boron (B)	**	0.49	1.13	1.8
Other Impurites	<0.3	<0.3	<0.3	<0.3

Table 4.3 Weight percent of each element in the sintered TMCs samples with different amount of reinforcements

According to chemical analysis results shown in Table 4.3, purities of all TMCs samples are very high. Aluminium comes from the impurity generated during the manufacturing process of titanium hydride powders reported by AG Materials Inc. The different weight percent of TiB_2 added into the matrix can be obtained by mass-mol equation using the value

in Table 4.3 assuming that all TiB_2 has already transformed into TiB. The calculation results didn't match with the practical additions, which were 1%, 3% and 5%, very well. One of the reasons should be that the testing part is not representative of the whole sample since only parts less than 0.2g are suitable to be tested by the ICP. Another reason should be the transformation from titanium diboride to titanium monoboride wasn't complete. Future WDS test, which is able to detect boron, needs to be carried out to determine the detailed amount of boron in the titanium composites.

4.4.2.2 XRD Spectrum

Figure 4.18 shows the comparison of XRD patterns between sintered TMCs with different amount of reinforcements. According to the image, nearly all titanium hydride powders have already disintegrated into titanium since the peak of TiH_2 is hardly detected in all composites. And, only the sample with 5% reinforcement shows apparent peaks of TiB compared with other ones. All titanium peaks match well between different samples.

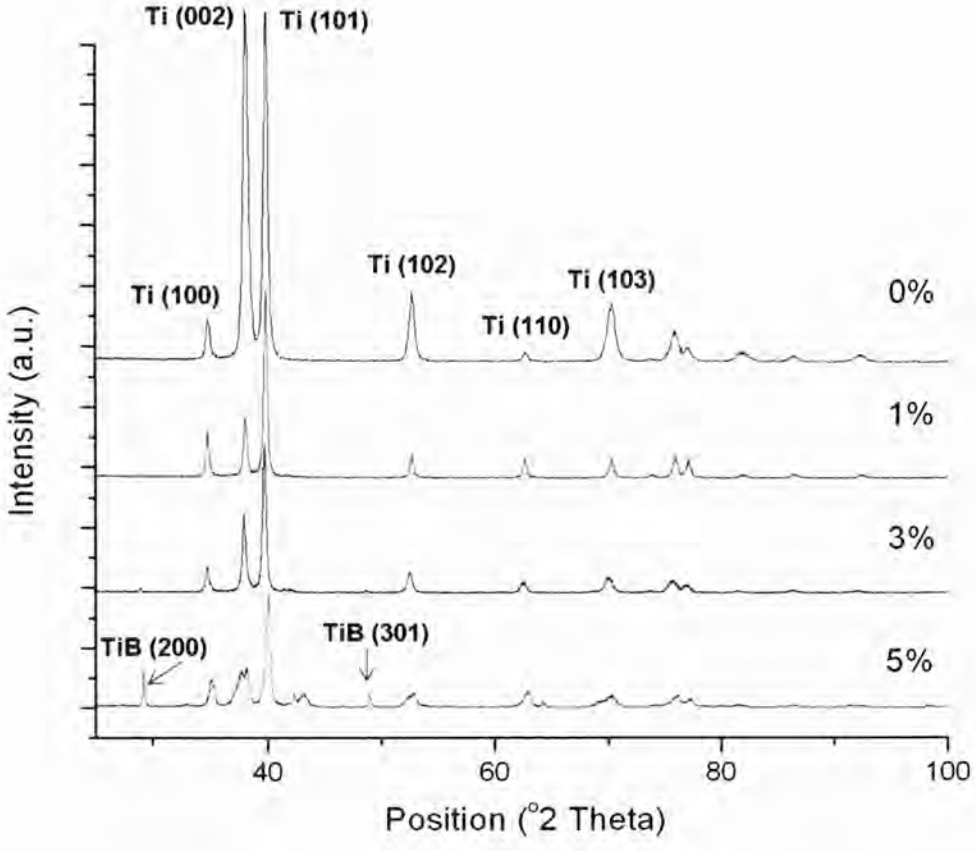
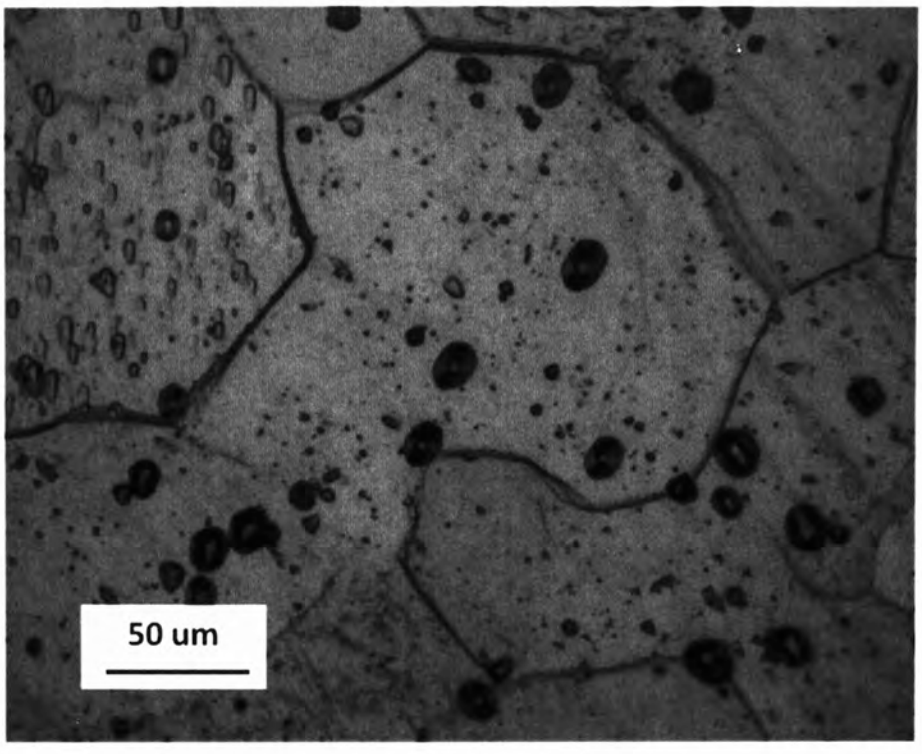


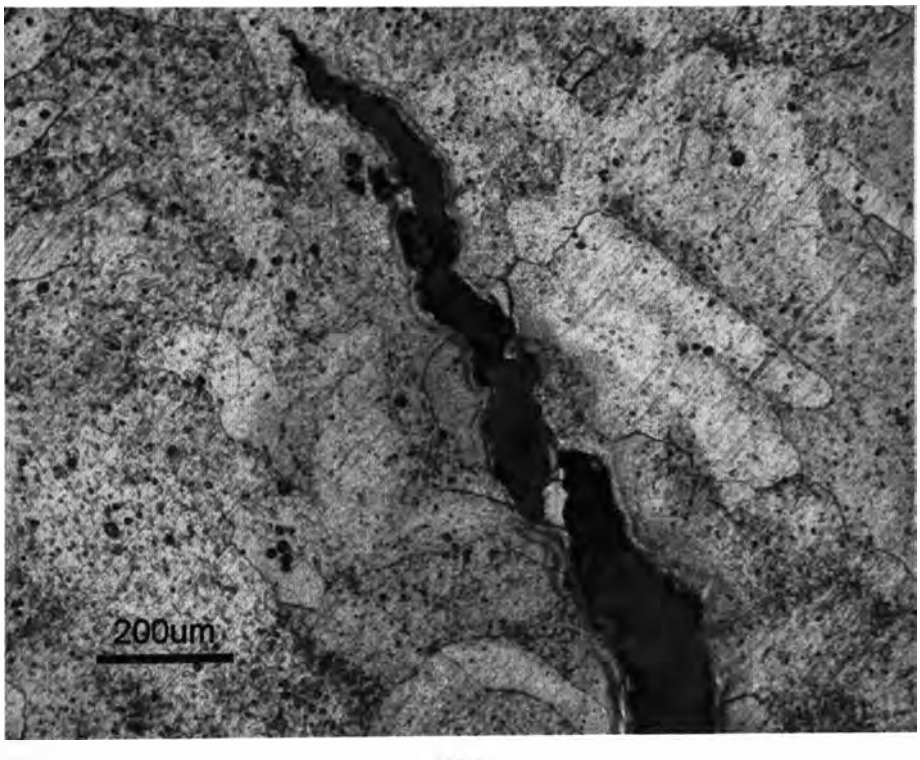
Figure 4.18 Comparison of XRD patterns between sintered TMCs samples with different amount of reinforcements

4.4.2.3 Optical Microscopy Results

Figures 4.19-4.22 represent cross-section structures after etching by Kroll's reagent of TMCs samples with different amount of reinforcements.



(a)



(b)

Figure 4.19 Optical microscopy images of TMCs samples without reinforcements: (a) Equiaxed structure and pores are observed (b) A crack cuts through the titanium grains

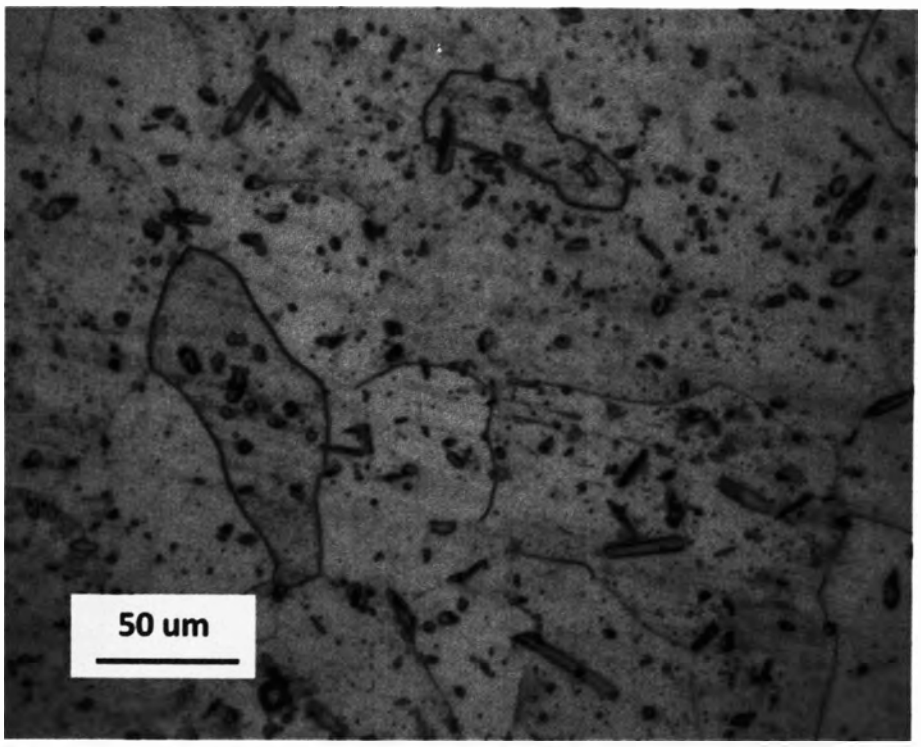


Figure 4.20 The optical microscopy image of TMCs samples with 1% reinforcements

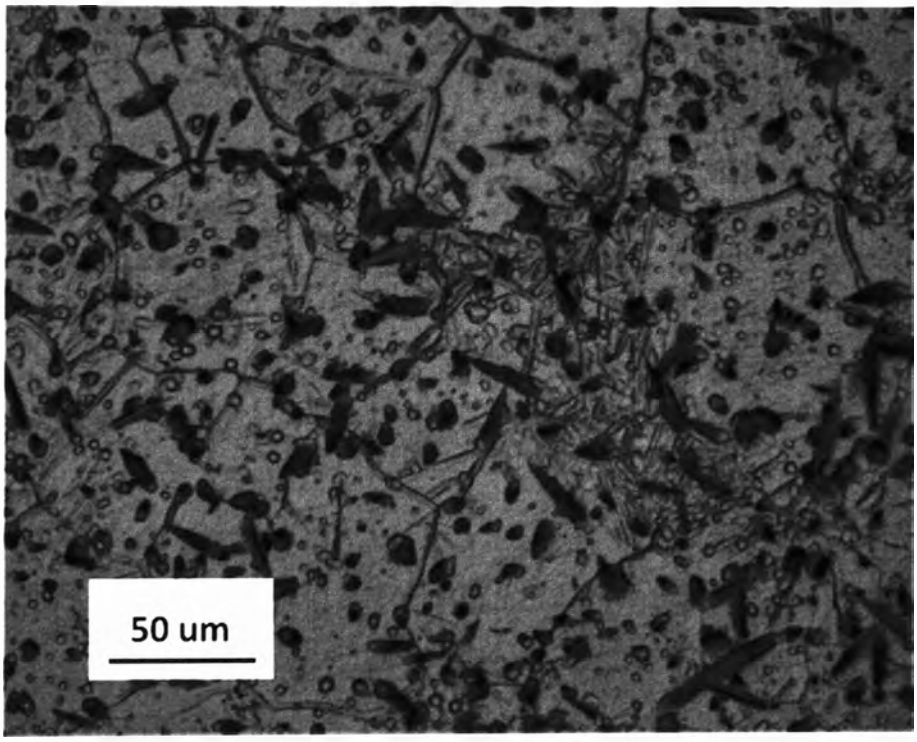
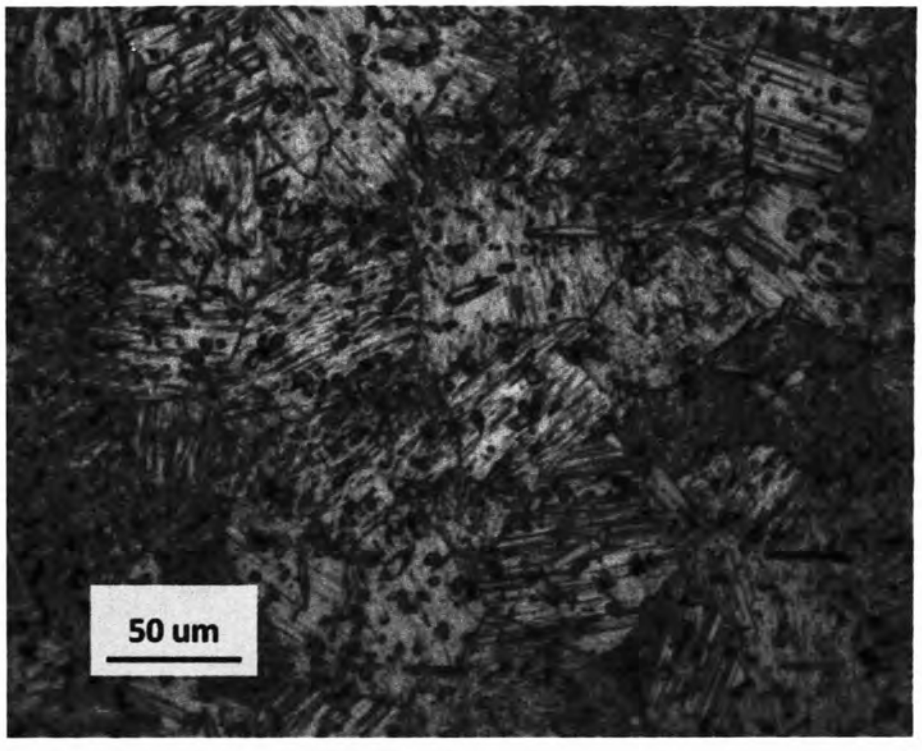
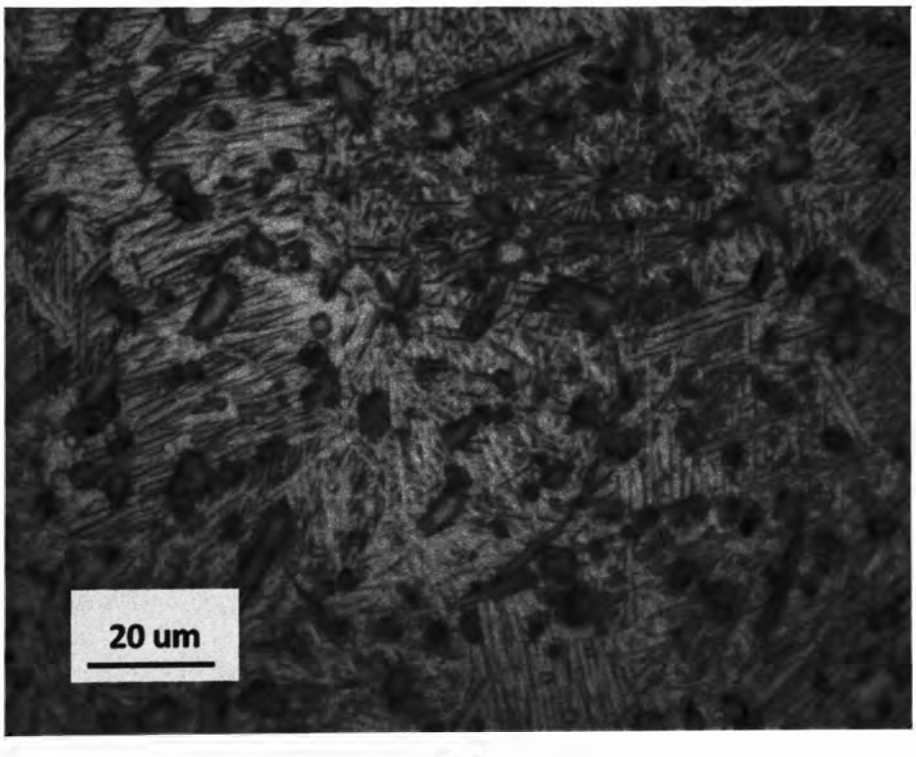


Figure 4.21 The optical microscopy image of TMCs samples with 3% reinforcements



(a)



(b)

Figure 4.22 Optical microscopy images of TMCs samples with 5% reinforcements: (a) Edge of the cross-section without the acicular structure (b) Inner part of the cross-section with the evidence of acicular structure

In Figure 4.19a, equiaxed alpha structures are detected for the pure Ti sample, with an average grain size of 200 micrometers. This should be due to the long furnace cooling time during the manufacturing process which allows more time for the grain growth. A small amount of porosities is detected both inside the grain and along the grain boundary. Figure 4.19b shows that one crack cuts through grains and it may be generated by the linkage of porosities. The reason for the linkage may be that before the furnace cooling process, some amount of the hydrogen was still trapped inside the pores. When the cooling process took place, the pressure inside pores was higher than the outer part as the temperature went down. The expansion of these pores resulted in the linkage and formation of the crack.

Equiaxed alpha structures are also observed in Figure 4.20, which shows the TMCs with 1% reinforcements and the average grain size has reduced to about 100 micrometers. And the amount of porosities in the sample is similar to that in the pure titanium one. TiB reinforcements randomly and evenly distribute in the composite and some of them are found inside the grain. The size of reinforcements is about 20-30 μm in length and several microns in width, which is much smaller than those used in commercial valves from Toyota Motor Corporation.

Both equiaxed and acicular structures are found in TMCs samples with 3% reinforcements in Figure 4.21. Acicular structures can be observed growing along the grain boundaries. Also, the grain size has reduced to about 50 μm.

OM images of TMCs with 5% reinforcements are shown in Figure 4.22. In Figure 4.22a, nearly no acicular structure can be detected at the edge of the cross-section area. But in the center part of the cross-section, which is shown in Figure 4.22b, acicular structures are found everywhere and equiaxed structures can hardly be found. Also, pores nearly disappear in this area. The size of grains has reduced to tens of microns or even smaller. Reasons for the different structures in different parts of the cross-section are still not clear and need to be investigated in the future research on boron effect.

With the increasing amount of reinforcements, the amount of acicular structures increases with the amount of equiaxed structures decreasing and the size of grains also decreases. Microstructure and tensile properties of Ti-6Al-4V with boron addition, which were reported by T. M. T. Godfrey [32], indicated that the refinement of the grain was achieved by increasing the amount of boron addition, which is similar to this project. But with the increasing boron addition, more equiaxed structures were found in the matrix, which is opposite to this project. Inconsistency of boron effect between their work and literatures were also reported. This phenomenon, including the unsolved boron effect in this project, still needs to be investigated in the future study.

4.4.2.4 SEM Results

Figures 4.23-4.26 show SEM images of the cross-section of TMCs samples with different amount of reinforcements after gold coating.

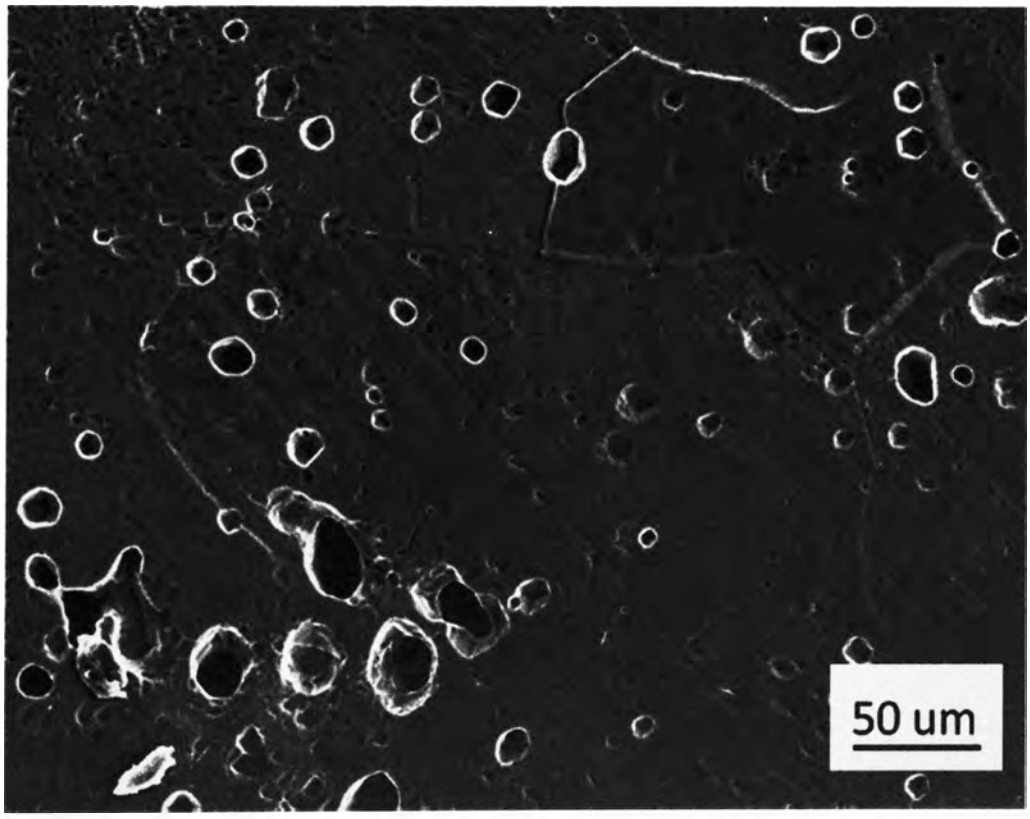


Figure 4.23 The SEM image of TMCs sample without reinforcements

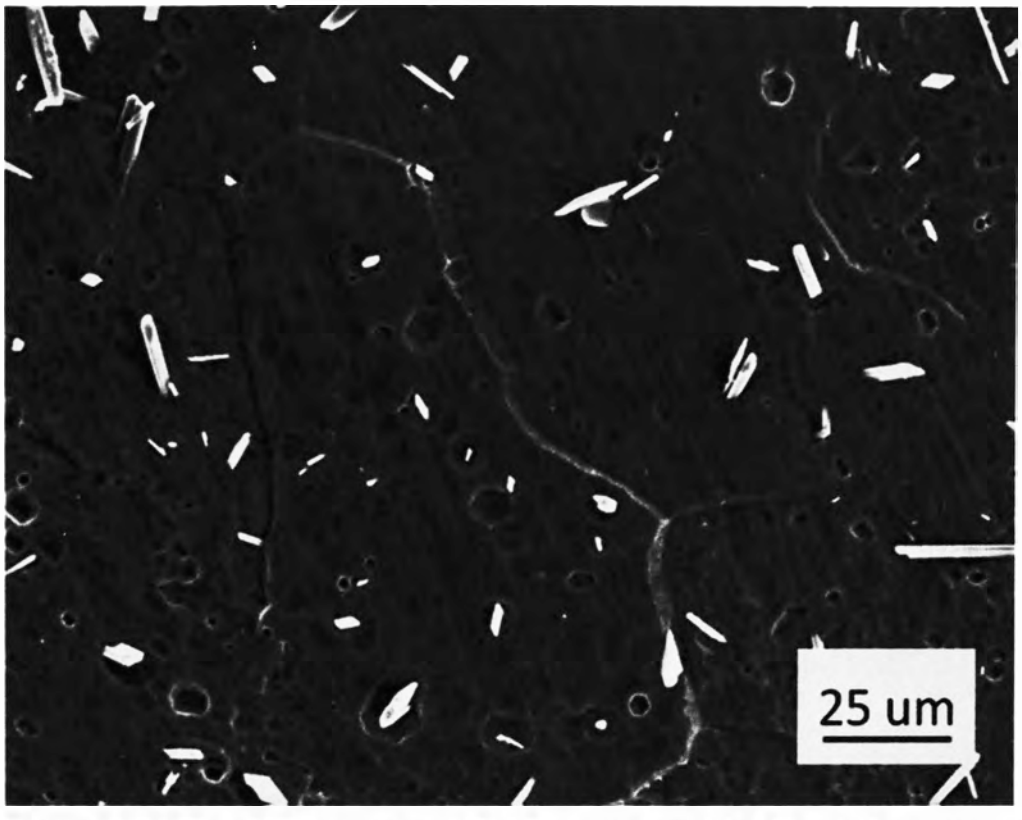


Figure 4.24 The SEM image of TMCs sample with 1% reinforcements

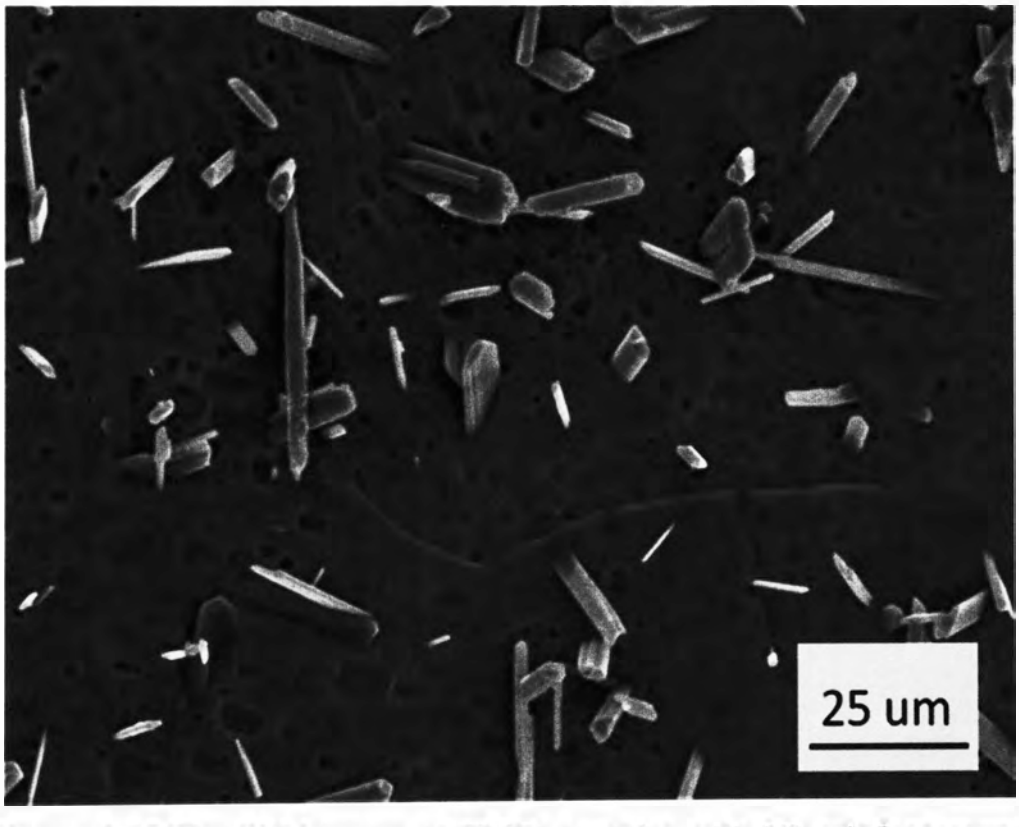
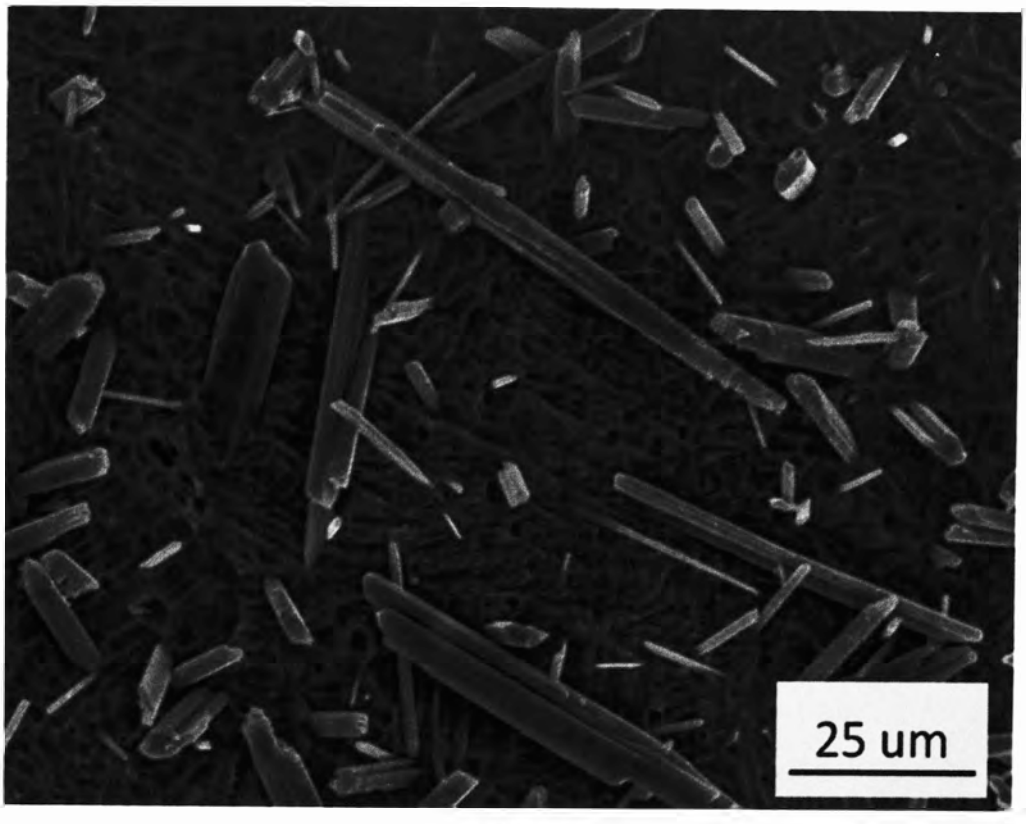
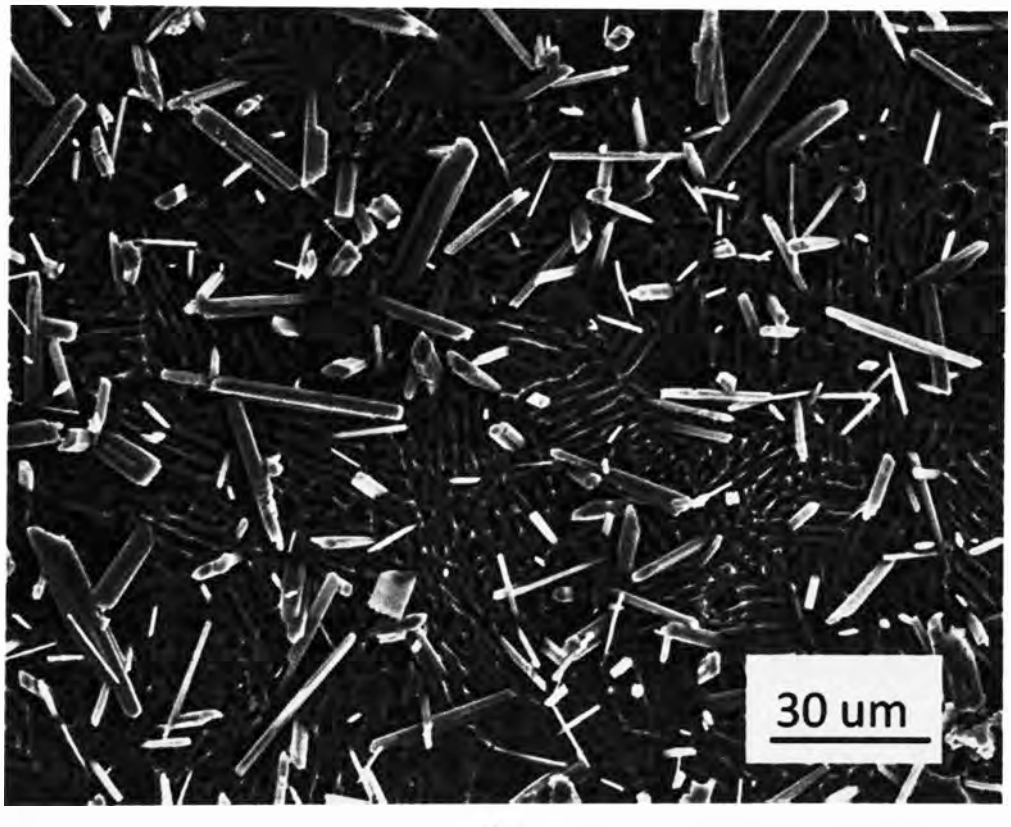


Figure 4.25 The SEM image of TMCs samples with 3% reinforcements



(a)



(b)

Figure 4.26 SEM images of TMCs samples with 5% reinforcements: (a) Large reinforcement can be detected (b) Acicular structure is evident through the matrix

In Figure 4.23, porosities and some unknown circular structures, which are proved to be titanium under EDS, are found both along the grain boundaries and inside the grains. Equiaxed alpha structures are evident in the image.

Same structures as those in Figure 4.23 are found in Figure 4.24, which represents the samples with 1% reinforcements. Whisker-like TiB reinforcements randomly distribute and are found both in the grain and along the grain boundary. A grain with the size of about 100 μm can be observed clearly. Some dents are also observed in the grain which is still unknown that how they formed. The average length of reinforcements is about 20-30 μm and the width of them is about several micrometers.

In TMCs samples with 3% reinforcements, dents are also found in the grain, which is shown in Figure 4.25. The average size of reinforcements grows a little bit and they randomly distribute in the equiaxed alpha grains as a part of the grain boundary can be easily observed in the image.

Figure 4.26 represents the TMCs samples with 5% reinforcements. In Figure 4.26a, it can be observed that the length of TiB reinforcements increases a lot, and they can no longer be defined as sub-micron size. Future size refinement needs to be carried out to make sure most of the reinforcements are in sub-micron and even nano-metric range. Nearly no equiaxed alpha structures can be found in Figure 4.26b, and acicular structures are evident all through the matrix.

In the literature [16], TMCs with acicular structures can have superior creep properties, higher fracture toughness values and slightly lower tensile and yield strengths at room and elevated temperature. For TMCs with equiaxed structures, they exhibit higher ductility and formability, superior low-cycle and high-cycle fatigue properties and slightly higher tensile and yield strengths at room and elevated temperature for equivalent heat treatment [16]. This means that by changing the amount of reinforcements and processing parameters, different mechanical properties can be obtained. As applied to the automobile industry, composites which have a better creep resistance and superior low-cycle and high-cycle

fatigue properties are preferred, so a combination of equiaxed and acicular structures in the composites may bring positive effect to the industry.

EDS facility equipped in the SEM has also been used to carry out the EDS testing on the composites samples to verify the composition of them. Since boron can not be detected by the EDS facility, only titanium peak was found in the pattern. No other apparent impurities were found in the pattern.

4.4.2.5 Hardness Results

In Figure 4.27, it can be concluded that TMCs sample with 5% of sub-micron and nano-metric reinforcement has the highest Vickers hardness value even compared with commercial exhaust valves from Toyota Motor Corporation. The hardness of the sample with 3% of reinforcement can be comparable with that of commercial valves. In this condition, the strengthening effect of sub-micron and nano-metric reinforcement to the pure titanium is the same or even better than that of micron reinforcement to titanium alloys. Scattering of the hardness results on composites in this project is much larger than that on commercial exhaust valves. This should be due to the porosities inside these manufactured composites.

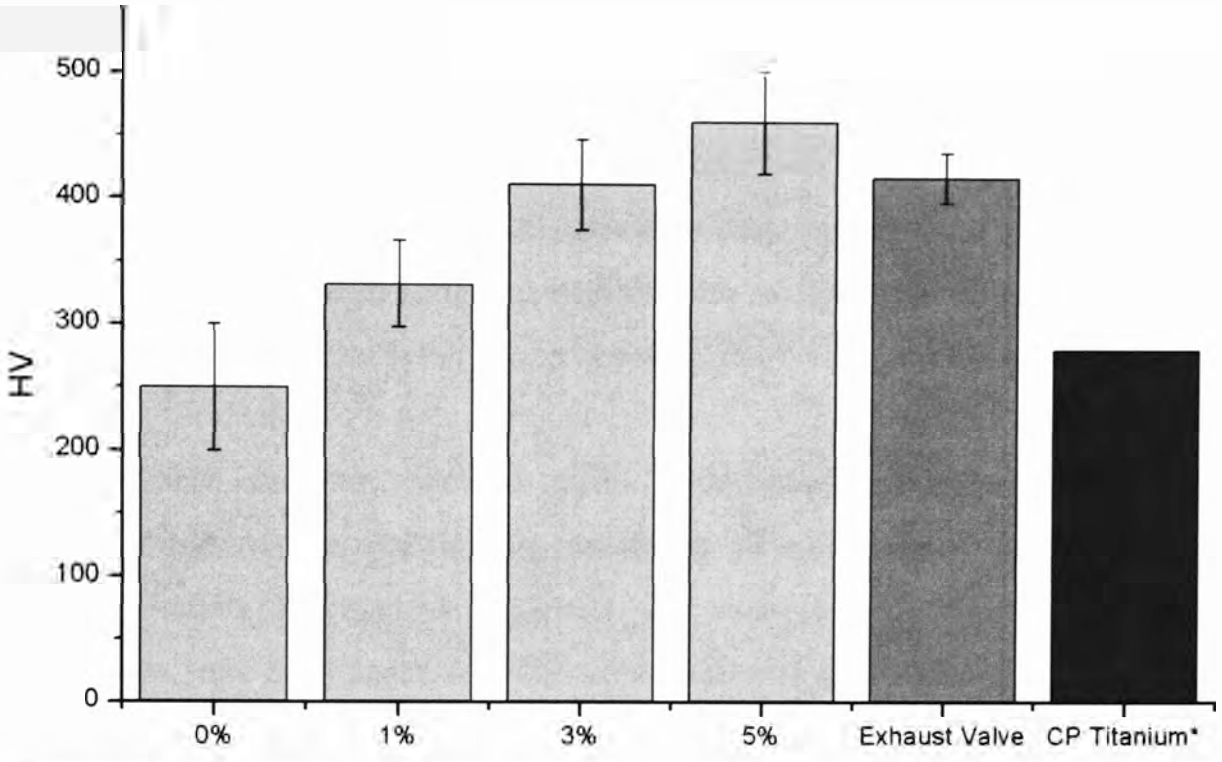


Figure 4.27 Comparison of Vickers hardness between sintered TMCs samples with different amount of reinforcements, commercial exhaust valves and CP titanium (* 99.0wt% Ti, Grade 4, Annealed) [30]

5 Conclusion

Titanium matrix composites with different amount of TiB reinforcements have been manufactured in this project, using a revised powder metallurgy process consisting of powder mixing, CIPing, degassing and HIPing. This revised process was designed to save fabrication steps and acquire better properties compared with conventional ones.

As the reference samples, titanium alloys composites exhaust valves, which were manufactured by conventional powder metallurgy process, were purchased from Toyota Motor Corporation. Mechanical properties and microstructure examinations on these exhaust valves have been described. According to the results, titanium matrix composites can have better mechanical properties than those of unreinforced alloys, but with the expense of the ductility.

Examinations on the starting materials, which were used to fabricate composites in this project, were also carried out. Dehydrogenation process of titanium hydride powders has been re-examined and validated by DSC testing.

In the manufacturing process of composites in this project, cracks were found all through the surfaces of TMCs samples when 2°C/min and 5°C/min heating rates were used during dehydrogenation and sintering processes. Cracks are easily generated if titanium hydride releases hydrogen too fast, which will cause the hydrogen embrittlement effect. So, a much slower heating rate is preferred in future studies. According to previous works [11, 18] and this project, different amount of hydrogen in the titanium hydride powders, different size of starting materials and reinforcements, different heating rate during degassing and sintering processes will all affect the final quality of products.

Only hardness testing was carried out on the manufactured titanium composites, and the comparison between commercial valves and composites reinforced with sub-micron ceramic particles in this project showed that composites with smaller particles

reinforcements have higher hardness value than those with larger reinforcements. The reason was still unclear.

In the study of microstructures of TMCs manufactured in this project, the amount of acicular structures in the titanium matrix increased with the increasing amount of reinforcements. This condition also resulted in the decreasing amount of equiaxed structures, decreasing size of grains and increasing size of reinforcements. According to the previous work by T. M. T. Godfrey [32], the refinement of the grain was achieved by increasing the amount of boron addition, which was similar to this project. But with the increasing boron addition, more equiaxed structures were found in the matrix, which was opposite to this project. The cause of the inconsistency was still unclear.

6 Future Work

(1) Size refinement of the starting reinforcements needs to be carried out by using high energy ball milling to make sure most of the TiB particles are in sub-micron and nano-metric size.

(2) In order to proceed on mechanical testing, cracks needs to be eliminated. Fast heating rate during the degassing and sintering process should be the main reason leading to the hydrogen embrittlement. In the future fabrication process, 0.5°C/min, 0.2°C/min and 0.1°C/min will be used individually as the heating rate from the dehydrogenation starting temperature, which is 400°C, to the sintering temperature (1300°C) instead of 5°C/min and 2°C/min used in this project. The other parameters will remain the same as those in this project.

(3) Hardness results of composites in this project showed that smaller reinforcements can help increase the hardness value of composites compared with larger ones. When cracks are not found in the manufactured samples, tensile testing is needed to further validate whether smaller size reinforcements can have better strengthening effect on composites than larger ones. Parameters used in the future tensile testing should be the same as those used on commercial exhaust valves in this project.

(4) More testing on mechanical properties of refined TMCs reinforced with sub-micron and nano-metric particles are needed, such as wear test, fatigue test etc., to make sure whether nanotechnology benefits the composites. Then the optimum amount of reinforcements needs to be acquired.

(5) Microstructures of refined composites samples needs to be examined using SEM and TEM. The reinforcement distribution and the boron effect on the structures transformation need to be found out to obtain the basic strengthening mechanism of sub-micron and nano-metric reinforcements.

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List of Figures

List of Tables