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**In-Situ Boron-Induced Grain Refinement and Its Impact on the
Metallurgical and Mechanical Properties of Ti6Al4V Alloy Processed
by Laser Powder Bed Fusion**

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To my family and people who are reading this page....

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In the early days of my PhD, I imagined this acknowledgment would be a simple conclusion, the last page before I finally closed the chapter of student life. But as I write these words, I realize this is not an ending but a reflection on a journey—one full of discovery, challenges, and growth. None of it would have been possible without the support of so many.

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ABSTRACT

This PhD thesis investigates the role of boron-modified Ti6Al4V alloys fabricated using Powder Bed Fusion – Laser Beam in achieving in-situ grain refinement and enhanced mechanical properties. Through the incorporation of both amorphous and crystalline boron, this research explores the resulting microstructural evolution, phase transformation, and mechanical performance. Key findings demonstrate that even a small addition of boron (0.1 wt.%) significantly refines the grain structure of Ti6Al4V alloys, transitioning from coarse, columnar grains to a more desirable equiaxed morphology. This refinement is particularly critical for overcoming the anisotropic mechanical properties commonly associated with additively manufactured titanium alloys.

Crystalline boron was found to be more effective than amorphous boron in promoting uniform grain refinement, densification, and improved mechanical properties. During solidification, the edge-to-edge matching mechanism between Boron particles and the β -phase played a crucial role in these improvements, enabling the crystalline boron-modified Ti6Al4V to consistently outperform its amorphous counterpart, especially at higher energy densities and longer laser exposure times.

The study also developed a novel Schmid factor algorithm to evaluate the influence of grain orientation and active slip systems on mechanical behaviour. This analysis revealed that boron-modified alloys, particularly those with crystalline boron, exhibited improved mechanical anisotropy, with more isotropic properties observed under 0° orientation.

Furthermore, the research emphasizes the importance of optimizing PBF-LB/M process parameters, with laser power and exposure time identified as key factors in controlling grain refinement and phase distribution. Crystalline boron-modified alloys demonstrated higher relative density, hardness, and more consistent mechanical properties, especially under higher power settings.

The strengthening mechanisms in boron-modified Ti6Al4V alloys were primarily attributed to grain refinement and structural strengthening, while the load-bearing effect of TiB particles played a minimal role. These findings offer a pathway for improving the mechanical performance of PBF-LB/M produced titanium alloys through controlled microstructural refinement.

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CHAPTER 1

INTRODUCTION

Titanium, the fourth most abundant structural metal in the Earth's crust, is known for its exceptional properties, including tensile strengths comparable to many steels, despite being only 60% as dense. These characteristics, combined with a high strength-to-weight ratio, excellent corrosion resistance, and the ability to endure elevated temperatures, make titanium alloys highly sought after across various industries (Boyer, 2010; M. J. Donachie, 2000; X. Yang & Liu, 1999). In particular, the aerospace sector heavily relies on titanium alloys due to these advantageous traits. However, while these alloys offer high ductility, strength, and thermal resilience, they also present significant challenges during machining (X. Yang & Liu, 1999). The material's inherent strength and low thermal conductivity lead to rapid tool wear, as heat accumulates during the machining process. At higher temperatures, titanium not only maintains its strength, which exacerbates tool degradation, but it also becomes more reactive, increasing the risk of contamination from foreign elements (Ezugwu & Wang, 1997). These factors contribute to the inefficiency of subtractive manufacturing processes for titanium, both in terms of time and material waste.

In the case of the F-22 Raptor, which is constructed using approximately 39% titanium, the quantity of titanium purchased is nearly ten times the amount that ultimately becomes part of the aircraft due to machining losses. This disparity is quantified by the aerospace industry through what is known as the "Buy-to-Fly" ratio (Seong et al., 2003). The buy-to-fly ratio highlights the significant material wastage that is typically encountered in the subtractive manufacturing process of titanium. While titanium offers several advantages over steel, such as superior strength-to-weight ratio and corrosion resistance, its widespread use is hindered by its high cost. A substantial portion of this expense stems from the difficulties associated with its fabrication. Additionally, the high rate of material wastage further escalates the cost of titanium components, limiting its usage to industries that can afford the investment despite the material's superior performance characteristics (M. J. Donachie, 2000).

To promote the broader application of titanium, it is essential to reduce fabrication costs by re-evaluating the manufacturing processes to enhance efficiency and significantly minimize material waste. Additive Manufacturing (AM) represents a promising technological advancement that addresses these challenges (Seong et al., 2003). In AM, components are fabricated from powders or wires through selective melting or sintering, constructing parts layer by layer (Bhattacharjee et al., 2017). This approach enables the creation of near-net-shape

components, which drastically reduces or eliminates both material waste and the associated machining expenses. Furthermore, AM offers substantial flexibility, making it possible to produce highly intricate and geometrically complex parts that are often unachievable with traditional manufacturing methods. The capability of AM to produce such complex geometries does not incur the typical penalties of extended machining times or increased material waste. Additionally, the adaptability of AM supports rapid prototyping, facilitating the swift iteration of design concepts. However, metal AM components often undergo complex thermal cycles, including directional heat extraction, repeated melting, and rapid solidification, which lead to heterogeneous microstructures that differ from those produced by traditional methods (S. M. Kelly & Kampe, 2004). These microstructural variations can result in heterogeneous properties, further compounded by defects like pores and rough surfaces, which are common in AM parts (M. W. Wu et al., 2016). Despite these challenges, AM remains an adaptable method for rapid prototyping and design iteration.

PBF-LB is a well-established powder bed fusion technique in additive manufacturing, which employs a laser beam to selectively melt layers of powder materials, including metals, polymers, and ceramics. In this research, the term PBF-LB/M specifically refers to metal powder bed fusion, where layers of metal powder are selectively melted by laser. Due to its higher precision, superior surface finish, and controlled operation in a noble gas environment compared to other metal additive manufacturing methods such as electron beam powder bed fusion (PBF-EB) or directed energy deposition (DED), PBF-LB/M has become a favoured technique for producing Ti6Al4V components. Ti6Al4V, often called the workhorse alloy, is the most commonly used titanium alloy in this process. Its widespread application is attributed to its excellent strength-to-weight ratio, corrosion resistance, and biocompatibility, making it particularly useful in aerospace, marine, and medical fields (M. J. Donachie, 2000). Consequently, Ti6Al4V is one of the most thoroughly researched materials in PBF-LB/M. However, challenges remain concerning the microstructural properties of Ti6Al4V parts produced by this method. The understanding of how PBF-LB/M influences the microstructural characteristics of as-built Ti6Al4V parts is still in its early stages and requires further investigation. Typically, the microstructure of Ti6Al4V produced by PBF-LB/M consists of columnar prior- β grains and fine acicular α' martensite, resulting from the high thermal gradients during the fabrication process (Thijs et al., 2010). However, limited studies have explored the mechanisms that govern the growth of these columnar and acicular grains during the PBF-LB/M processing of Ti6Al4V. A deeper understanding of the cyclic thermal effects on microstructure evolution in as-built Ti6Al4V components is crucial and will contribute significantly to the broader knowledge of microstructure regulation in PBF-LB/M processes. Additionally, a significant challenge lies in the limited understanding of how microstructures evolve in Ti6Al4V produced via PBF-LB/M under dynamic working conditions. Conventional mechanical tests are typically conducted in quasi-static environments with strain rates below 10^{-3} s^{-1} (Ouellet et al., 2006). In contrast, dynamic conditions occur when the strain rate is high enough for dislocation speeds to match or exceed the shear wave velocity, commonly reported in the range of 10^2 to 10^4 s^{-1} (Q. Li et al., 2004; Sassi et al., 2019). The deformation behaviour

under these strain rates differs significantly from quasi-static conditions, as high strain rates activate thermally driven mechanisms, leading to adiabatic microstructural changes (Odeshi et al., 2005). Dynamic deformation is relevant in various industrial applications, such as aircraft landing gears, bird strikes, car crashes, or ballistic impact armour. Therefore, understanding how Ti6Al4V manufactured via PBF-LB/M responds to dynamic deformation is crucial for its effective application, particularly in ensuring safety standards. Another challenge with Ti6Al4V produced by PBF-LB/M is how its mechanical properties compare to those of conventionally manufactured materials. The rapid cooling rates and layer-by-layer deposition characteristic of PBF-LB/M contribute to the formation of non-equilibrium phases and anisotropic behaviour (Khan et al., 2007; Simonelli et al., 2014; M. W. Wu et al., 2016). The martensitic microstructure results in high hardness and strength, but at the cost of reduced ductility. Therefore, heat treatments are necessary to achieve a balance of properties similar to those of bulk materials. Vrancken and Thijs (Vrancken et al., 2012) observed that heat treatments for as-built PBF-LB/M Ti6Al4V components need to be specifically adjusted due to the distinct initial microstructure. Conventional heat treatments like milling, duplexing, and beta annealing have been found ineffective in significantly enhancing the performance of PBF-LB/M Ti6Al4V parts.

1.1 Motivation

The justification for employing additive manufacturing processes, particularly PBF-LB/M, stems from their ability to produce intricate geometries and complex topologies that are unachievable through conventional fabrication methods. By building parts layer by layer, additive manufacturing techniques offer considerable advantages, such as reduced material waste, enhanced design flexibility, and more efficient use of materials. However, the mechanical performance of components produced through additive manufacturing, especially Ti6Al4V, remains a topic of ongoing research due to the complex microstructures formed during the process. Thus, a comprehensive understanding of the microstructural evolution during the PBF-LB/M process is essential for optimizing the performance of final parts, particularly in demanding applications like aerospace and biomedical fields.

Microstructure has a profound influence on the mechanical properties of metallic materials, such as strength, ductility, and fatigue resistance. In the case of Ti6Al4V produced via PBF-LB/M, the rapid cooling rates and thermal gradients result in coarse columnar grains and martensitic phases, which may not provide the optimal balance of mechanical properties required for critical applications. Consequently, strategies for refining the grain structure and tailoring the phase composition are crucial.

Grain refinement is an established metallurgical process that has been widely used to achieve desirable microstructures in cast materials, directly affecting properties like yield strength, hardness, and ductility (Crossley, 1983; Hansen, 2004). Grain refinement can be achieved through nucleant and solute addition, which introduces new nucleation sites and promotes constitutional supercooling, respectively. Nucleant particles, when introduced into the liquid

metal, increase the number of grains formed, reducing the overall grain size. Solute contribute by restricting the growth of columnar grains through supercooling, allowing more nucleation events to occur within the melt. Using inoculations and solutes in combination provides an optimized grain refinement strategy, leading to more homogeneous and fine-grained structures.

Among the strategies for grain refinement, the addition of alloying elements like boron has gained attention for its potential to promote in-situ grain refinement by forming titanium borides that act as nucleation sites during solidification. The application of boron for grain refinement in Ti6Al4V presents a promising avenue for improving the material's mechanical performance. The ability of boron to refine grains and alter the microstructure could lead to significant enhancements in both static and dynamic properties, particularly in components subjected to high stress or fatigue conditions. While boron has shown promise in traditional titanium alloy processing, its behaviour and effects within the PBF-LB/M process are not well understood. Therefore, investigating the role of boron in PBF-LB/M Ti6Al4V parts could yield valuable insights into enhancing the structural integrity and reliability of AM-fabricated titanium components.

Given the industrial demand for high-performance materials in aerospace, biomedical, and defence sectors, understanding and controlling microstructural evolution in AM-processed Ti6Al4V is crucial. This research aims to address these gaps by exploring the effects of trace boron addition on grain refinement and microstructure control in PBF-LB/M-produced Ti6Al4V, thus contributing to the broader advancement of AM technologies for high-performance applications.

In particular, the motivation for this research is strongly aligned with the growing demand for advanced structural materials in the defence sector. Titanium alloys, and specifically Ti6Al4V, are widely used in military aircraft, missile systems, and space platforms due to their exceptional specific strength, corrosion resistance, and thermal stability. Recent advancements in additive manufacturing have enabled the production of complex titanium components that were previously unachievable, with significant benefits in terms of weight reduction, assembly simplification, and performance optimization. For instance, Airbus has successfully used PBF-LB/M technology to manufacture titanium brackets for the A350 XWB aircraft, achieving notable weight savings and design flexibility. In the defence domain, companies such as Lockheed Martin, Raytheon, and SpaceX have adopted PBF-LB/M-produced Ti6Al4V components in critical systems, including jet engine parts, missile casings, and rocket thrusters, where mechanical integrity under extreme loading and thermal conditions is essential.

However, these applications impose stringent requirements on the consistency and reliability of material properties, particularly fatigue resistance and isotropic strength, which are often limited by the coarse, columnar microstructures formed during conventional PBF-LB/M processing. Therefore, this research aims to develop and validate a boron-modified Ti6Al4V alloy system capable of producing fully refined, equiaxed microstructures with enhanced

mechanical performance. By systematically investigating the effects of nanosized boron addition and optimizing processing strategies, this study directly contributes to advancing the material solutions required for next-generation defence platforms, including aircraft, missiles, and space systems.

1.2 Objectives

The primary aim of this research is to investigate the potential of in-situ grain refinement in Ti6Al4V produced by PBF-LB/M through the addition of boron. To achieve this overarching goal, the following specific objectives are defined:

1. Investigating direct mixing method to achieve homogeneously mixed graphite flake – Ti6Al4V composite powder feedstock to produce in situ TiB reinforced Ti6Al4V alloy produced by PBF-LB/M.
2. To determine the optimal boron concentration required for effective grain refinement in Ti6Al4V.
3. To study the combined effect of boron crystallinity and content on the microstructural evolution of Ti6Al4V alloys produced via rapid solidification.
4. To optimize PBF-LB/M processing parameters for achieving the desired microstructure and mechanical properties in boron-modified Ti6Al4V.
5. To investigate the role of Boron and/or TiB formed during the PBF-LB/M process in promoting nucleation and grain growth.
6. To analyse the microstructural evolution in boron-modified Ti6Al4V alloys fabricated via PBF-LB/M.
7. To assess the mechanical properties of Ti6Al4V modified with different boron crystallinities, produced via PBF-LB/M.

1.3 Thesis Outline

Chapter 2 provides a comprehensive review of the physical metallurgy of titanium, with a particular focus on Ti6Al4V, and boron-modified titanium alloys, produced via traditional manufacturing and additive manufacturing methods. It also reviews the current state of additive manufacturing for titanium alloys. Chapter 3 describes the materials and experimental procedures used in this research. This includes the preparation of Ti6Al4V samples, boron-modified alloy production methods, as well as the PBF-LB/M process parameters. The chapter also covers the methodologies for post-processing and microstructural analysis, including EBSD, XRD, and mechanical testing. Chapter 4 focuses on the investigation of boron-induced grain refinement in Ti6Al4V, comparing results from arc melting trials and powder-free surface laser glazing technique. This chapter discusses the optimal boron content for grain refinement and the effects of boron on the microstructure of the alloy, providing insights into the effectiveness of boron additions in traditional and PBF-LB/M processes. Chapter 5 discusses the preparation and characterization of composite powders for PBF-LB/M. This chapter explores the process of creating boron-modified Ti6Al4V powders and analyses their physical and chemical properties, including powder morphology, particle size distribution, and the distribution of boron within the powder. Chapter 6 presents the findings on boron-induced

microstructural manipulation of Ti6Al4V fabricated by PBF-LB/M. This chapter examines the formation of titanium borides (TiB) during the PBF-LB/M process, the resulting grain refinement, and the effects on phase distribution and crystallographic texture. Chapter 7 discusses the mechanical properties of boron-modified Ti6Al4V alloys produced by PBF-LB/M. This chapter presents tensile strength in longitudinal and transverse direction comparing boron-modified alloys with unmodified Ti6Al4V. The effects of crystallinity of boron, and grain refinement on mechanical performance are explored in detail. Chapter 8 summarizes the key conclusions of the research and provides recommendations for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 Titanium and Titanium Alloys

Titanium ranks as the ninth most abundant element and the fourth most plentiful structural metal in the Earth's crust—following aluminium, iron, and magnesium (Imam et al., 2010; Leyens & Peters, 2006; Lütjering & Williams, 2003). It offers several benefits, including excellent corrosion resistance, favourable mechanical properties, and a low density, i.e., a high specific strength. Its density stands at 4.51g/cm^3 , which is notably favourable compared to other structural metals. Titanium predominantly exists in the form of rutile (TiO_2) and ilmenite (FeTiO_3), with these ores being discovered in the late 18th century. Ilmenite is primarily located in Russia's Ilmeny mountains, while rutile is sourced from beach sands in India, Australia, and Mexico (Leyens & Peters, 2006). The name "titanium" is derived from Greek mythology, referencing the Titans, a formidable race of divine beings who, despite their power, were despised by their father and thus imprisoned in the Earth's crust, akin to titanium ore. Beyond rutile and ilmenite, numerous other titanium minerals exist. Rutile, anatase, and brookite share the same chemical formula (TiO_2) but differ in crystal structure. These three minerals contain a high titanium content, approximately 95 weight percent TiO_2 , whereas ilmenite's titanium content ranges from 40 to 65 weight percent.

Extracting pure titanium from its minerals is challenging due to its high reactivity with oxygen. As a result, an effective extraction method was only developed in the mid-20th century. This method, known as Kroll's process, produces titanium in a form referred to as titanium sponge because of its spongy and porous appearance. The intricate nature of this batch process contributes to titanium being more expensive than metals like steel. Additionally, titanium ores are not found in high concentrations (Leyens & Peters, 2006), further driving up the cost. Titanium alloys are renowned for their excellent specific strength relative to other structural alloys, surpassed only by carbon fiber reinforced polymer (CFRP). Titanium alloys can be used at temperatures up to 580°C (as in the alloy Ti834) before a brittle surface layer called α -case forms, whereas the alloy Ti6Al4V has a maximum service temperature of 350°C (Leyens & Peters, 2006; Welsch et al., 1993). For applications requiring higher temperatures, Ni-based alloys are suitable. At even higher temperatures, titanium-aluminide alloys such as TiAl are viable alternatives, particularly in turbine applications.

2.1.1 Titanium Crystal Structure

Titanium can exhibit two types of crystal structures; namely, body-centered cubic (BCC) and hexagonal close-packed (HCP). For commercially pure (CP) titanium, an allotropic transformation occurs from BCC to HCP. The BCC phase is referred to as the β phase, while the HCP phase is known as the α phase (Leyens & Peters, 2006). The temperature at which this phase transformation occurs (882 °C for pure titanium) is crucial for various thermomechanical processes and heat treatments of different titanium alloys. Moreover, the diffusion rates are strongly influenced by these two crystal structures (Leyens & Peters, 2006), affecting the texture. A high concentration of the α phase, characterized by numerous HCP crystals, increases the alloy's susceptibility to anisotropy due to the inherent anisotropy of the HCP crystal structure. For example, when an HCP crystal is subjected to a load perpendicular to the basal plane (0002), elastic modulus is 145 GPa, whereas it is only 100 GPa when the load is parallel to the basal plane (Leyens & Peters, 2006). Figure 2-1 shows the atomic unit cell of the HCP α -titanium on the left and the BCC β -titanium on the right, along with their most densely packed planes and directions highlighted. The BCC structure contains two atoms per unit cell, while the HCP structure contains six atoms per unit cell (Callister & Rethwisch, 2000). The atomic packing factor is marginally higher in HCP, being 0.74 compared to BCC with 0.68. Figure 2-1 illustrates some of the potential slip planes in both BCC and HCP structures. In the case of BCC, other potential slip planes include the $\{211\}$ and $\{321\}$ families, which are activated depending on the temperature (Callister & Rethwisch, 2000). The HCP structure has three distinct families that can form slip systems: $\{0001\}$, $\{10\bar{1}0\}$, and $\{10\bar{1}1\}$, with the slip direction being $\langle 11\bar{2}0 \rangle$. The activation of these slip systems is also temperature-dependent (Bridier et al., 2005; Callister & Rethwisch, 2000). BCC structures can have between 12 and 24 slip systems, while HCP structures have fewer, ranging from 3 to 6. This difference contributes to HCP metals being more brittle compared to BCC metals.

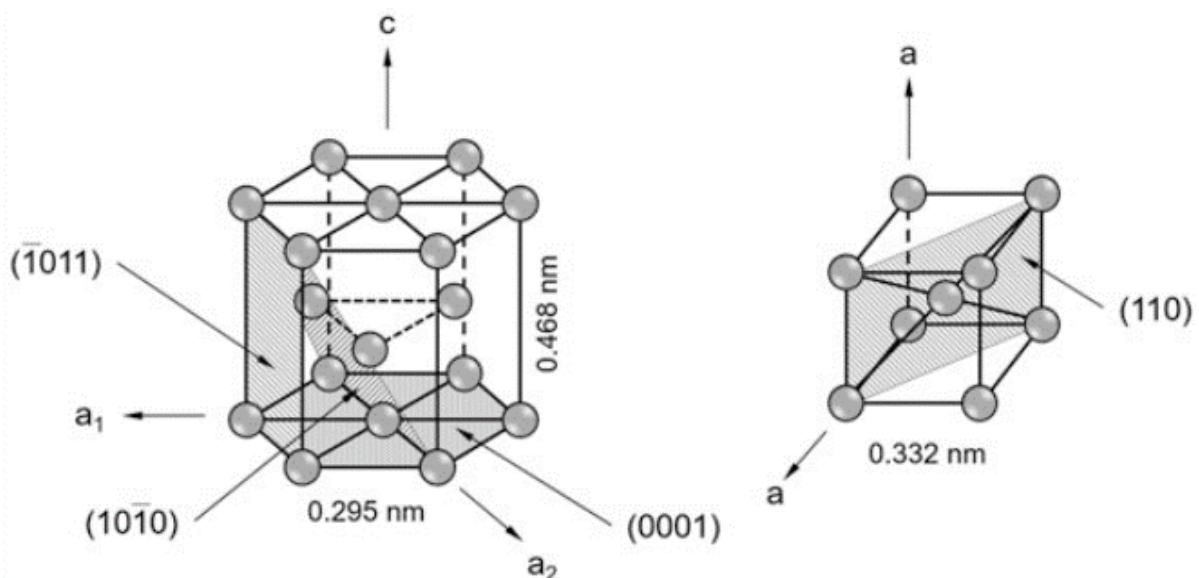


Figure 2-1 Crystal structure of HCP α -titanium on the left and BCC β -titanium phase on the right (Leyens & Peters, 2006).

2.1.2 The Classification of Titanium Alloys

Titanium alloys are broadly divided into three categories: α , $\alpha+\beta$, and β alloys, based on the presence of α and β phases at room temperature (Neikter et al., 2018). These categories feature varying levels of β -stabilizing elements, illustrated in Figure 2-2(a). An increase in the β -stabilizer shifts the β -phase field to lower temperatures, while an increase in the α -stabilizer extends the α -phase field to higher temperatures (Leyens & Peters, 2006). Additionally, titanium alloys can be classified as near- α alloys and near (metastable) β alloys. Elements stabilizing the β -phase include V, Mo, Nb, Ta, Fe, Mn, Cr, Ni, Cu, Si, and H (Imam et al., 2010; Neikter et al., 2018), with the first four being isomorphous β -stabilizers and the others eutectoid β stabilizers. High additions of eutectoid β stabilizers can lead to the formation of Ti_xA_y type compounds with titanium. Elements stabilizing the α -phase are Al, O, N, and C. Elements such as Zr and Sn are neutral stabilizers as they do not affect either the α or β phase. When cooling from $\beta \rightarrow \alpha$ phase, the densest $\{110\}$ planes transition to the basal planes $\{0001\}$. This phase transformation induces distortion among the atoms (Figure 2-2(b)) due to the larger distance between the basal planes in the α -phase compared to the $\{110\}$ planes in the β -phase (Leyens & Peters, 2006). For the HCP structure, this results in a contraction of the c-axis relative to the a-axis, leading to c/a ratio less than the ideal HCP atomic packing. Consequently, the volume slightly increases during the $\beta \rightarrow \alpha$ transformation (Leyens & Peters, 2006). This phase transformation follows Burger's orientation relationship: $\{0001\}_\alpha \parallel \{110\}_\beta$ and $\langle 1120 \rangle_\alpha \parallel \langle 111 \rangle_\beta$ (S. Al-Bermani, 2011; Lütjering & Williams, 2003). The slip directions and slip planes create 12 possible α variants for each β orientation. Diffusion properties differ between the phases. The lower diffusion rate in the denser HCP structure compared to the less dense BCC structure results in phase-dependent diffusion rates, affecting the overall microstructure.

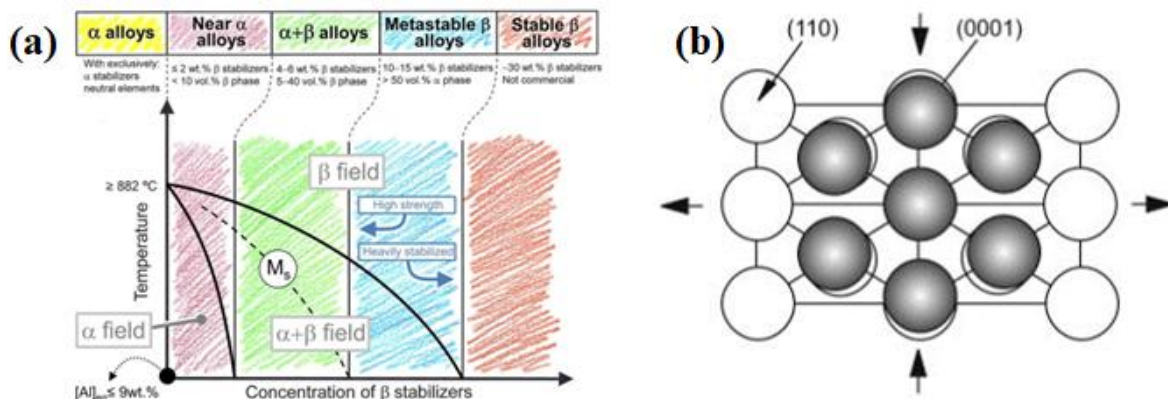


Figure 2-2 (a) Phase diagram for titanium illustrating various alloy categories: α , $\alpha+\beta$, and β alloys, distinguished by the quantity of β stabilizers present (Williams, 2013); b) atomic distortions from $\beta \rightarrow \alpha$ phase transformation arise because the spacing between the $\{0001\}$ planes is greater than the equivalent distance between the $\{110\}$ planes (Leyens & Peters, 2006).

2.1.3 Mechanical Properties of Titanium Alloys

Both the choice of alloying elements and the way the material is processed play key roles in shaping the mechanical characteristics of titanium alloys. Alloying primarily boosts strength through solid solution strengthening and affects most physical properties—such as density,

elastic modulus, and coefficient of thermal expansion—while also greatly influencing the material's resistance to corrosion and oxidation. However, incorporating or having interstitial elements (mainly C, O, and N) can enhance strength (see Figure 2-3(a)) at the risk of significantly lowering ductility (see Figure 2-3(b)). Beyond alloying, processing methods allow careful management of the α and β phases, which can be adjusted by applying various thermomechanical treatments (M. J. Donachie, 2000; Leyens & Peters, 2006; Lütjering & Williams, 2003).

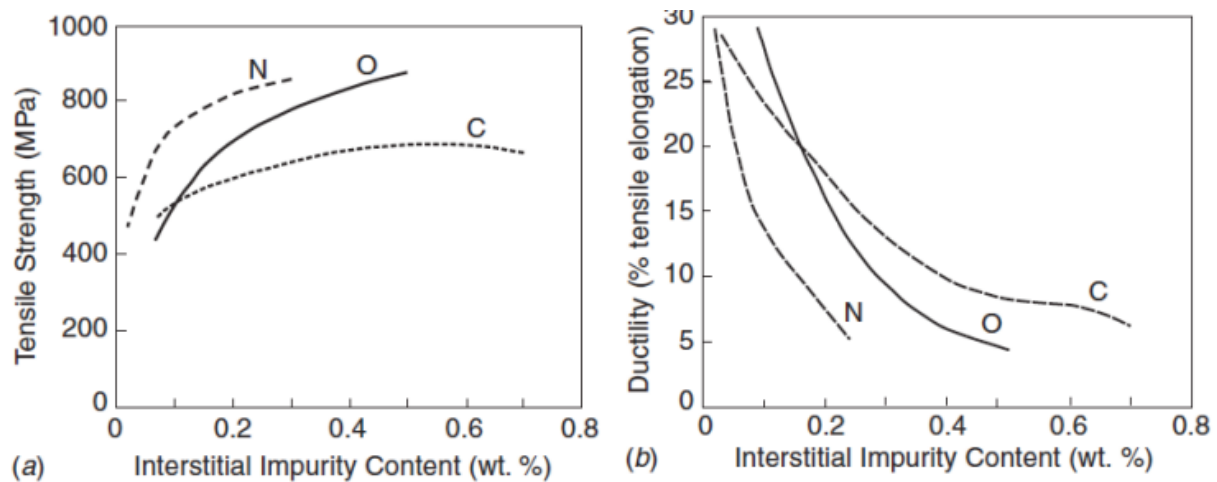


Figure 2-3 Diagrams showing how interstitial additions (C, N, O) influence (a) the tensile strength and (b) the ductility of CP-Ti (M. J. Donachie, 2000).

2.1.3.1 Tensile Properties

Under standard room temperature conditions, conventional titanium alloys typically achieve yield strengths of about 800-1200 MPa, regardless of the condition of material. Among these values, around 50-90% of that strength can still be maintained at elevated temperatures (93-530°C) (M. J. Donachie, 2000). It is widely recognized that, in most scenarios, cast alloys have lower tensile properties than their wrought counterparts. However, post-casting processes such as HIP and heat treatments can enable cast alloys to reach yield and ultimate tensile strengths on par with wrought alloys (M. J. Donachie, 2000; Leyens & Peters, 2006; Nastac et al., 2006). It is also known that tensile strength values can vary significantly when contrasting cast and wrought materials. This variation underlines that, apart from processing techniques, alloying elements also impact the tensile characteristics of titanium alloys. In fact, it has been shown that around 60% of the fluctuation in mechanical properties comes from common alloying additions such as interstitials (C, H, N, O) and residual iron (Fe) (Chong & Douglas, 1992; Nastac et al., 2006). Specifically, increasing oxygen content by 0.05 wt.% boosts the ultimate tensile strength by roughly 60 MPa, while the same amount of nitrogen or carbon raises it by about 125 MPa and 35 MPa, respectively. By contrast, adding 0.05 wt.% Fe only enhances the strength by 10 MPa, akin to the effect of hydrogen (Moiseyev, 2005). Consequently, hydrogen can be regarded as a key element that significantly influences mechanical performance (Nastac et al., 2006).

2.1.3.2 Fracture Toughness

In the aerospace field, it is typical to use a fail-to-safety philosophy when designing components. This approach usually follows a damage tolerance principle, which serves to link the presence of any flaws to the condition of the material. Within this framework, the concept of damage tolerance is referred to as fracture toughness (K_{IC}), a term used to describe how a material behaves once cracks reach a critical size and bring about uncontrollable crack propagation (Dieter & Bacon, 1988). Compared to steels, titanium alloys possess roughly half the fracture toughness, although these values can vary by factors of two or three among different titanium alloys. The reason behind this variation is that fracture toughness of titanium alloys depends significantly on their alloying elements, microstructure, texture, and the surrounding environment. Research indicates that oxygen levels exceeding 0.20 wt.% and hydrogen content greater than 150 ppm can greatly diminish fracture toughness, so it is essential to keep these contents low to maintain higher toughness. Beyond chemical composition, the microstructure formed during processing also plays a major role. For instance, alloys that develop a transformed β structure—namely α lamellar microstructures—often show enhanced toughness in comparison to their equiaxed counterparts. A useful example lies in the difference between cast and wrought Ti6Al4V. Observations reveal that cast Ti6Al4V demonstrates higher fracture toughness than its wrought counterpart. This improved performance in cast titanium alloys stems from their coarse lamellar microstructures (i.e., coarser α colonies), which can divert advancing cracks due to the unique texture of α colonies. As a result, the crack propagation rate is slower, requiring additional energy and ultimately producing a rougher crack path (M. J. Donachie, 2000; Leyens & Peters, 2006; Lütjering & Williams, 2003).

2.1.3.3 Fatigue Strength

Fatigue is essentially a way to gauge how well a material endures when subjected to repeated loading. One can look at it in two main stages: (i) the initiation of a fatigue crack and (ii) the propagation rate of any crack that already exists. Fatigue failures typically come in two forms: low cycle fatigue (LCF), where the failure occurs between fewer than 10^4 and up to 10^5 cycles, and high cycle fatigue (HCF), where the failure happens at more than 10^6 cycles (Dieter & Bacon, 1988). For most titanium alloys, fatigue behaviour is highly sensitive to factors like the chemical composition of the alloy, its microstructure, the environment, the temperature during testing, and the way the load is applied (M. J. Donachie, 2000; Leyens & Peters, 2006; Lütjering & Williams, 2003). When it comes to commercially pure titanium (CP-Ti), its fatigue strength mainly hinges on things like grain size, the level of interstitials, and the extent of cold work. For instance, cutting the α grain size down from 110 μm to about 6 μm can boost HCF by roughly 30% in CP-Ti. Moreover, raising the oxygen content or increasing the work-hardening rate can also improve fatigue strength (M. J. Donachie, 2000; Leyens & Peters, 2006). Consequently, one can argue that the HCF of CP-Ti is strongly tied to its interstitial content—much like its tensile properties.

For near- α and $\alpha+\beta$ titanium alloys, in addition to the aforementioned factors, the fatigue strength is also influenced by how the α and β phases are arranged and shaped (Lütjering &

Williams, 2003). Figure 2.9 displays typical LCF properties for Ti6Al4V in both cast and wrought conditions. From this, it is evident that cast Ti6Al4V exhibits a lower fatigue life than its wrought counterpart when strain ranges ($\Delta\epsilon$) go above 1%. Yet, at strain ranges below 1% and at 370°C, the cast and wrought forms of Ti6Al4V reveal quite similar LCF strengths (M. J. Donachie, 2000). Key microstructural elements that impact fatigue strength in titanium alloys include the size of the prior β grains, the dimensions of the α colonies, and the thickness of α laths in lamellar microstructures. Figure 2-4 also shows that cast Ti6Al4V, featuring coarser α lamellar structures, tends to have lower fatigue strength than wrought Ti6Al4V. This dip in strength can be traced back to the bigger α colony size in cast alloys, which effectively lengthens the slip path and thus reduces fatigue strength (Lütjering, 1998; Lütjering & Williams, 2007). Another set of factors influencing fatigue strength involves the surrounding environment, such as the atmosphere and temperature. It has been noted that CP-Ti achieves a longer HCF life in a vacuum than in argon, and that performance drops even further in air (Ismarrubie & Sugano, 2004). As for Ti6Al4V, its LCF life is higher in a vacuum than in air since crack initiation is significantly delayed. Research on Ti-6246 has shown that the location where fatigue cracks get started can change depending on the environment—shifting from the α/β interface in air to within the α laths in a vacuum (Demulsant & Mendez, 1996). Moreover, it was noted that in cast titanium alloys, fatigue cracks often originate by shearing across an α colony, shearing along the boundary α phase between grains, or at pores (Demulsant & Mendez, 1996).

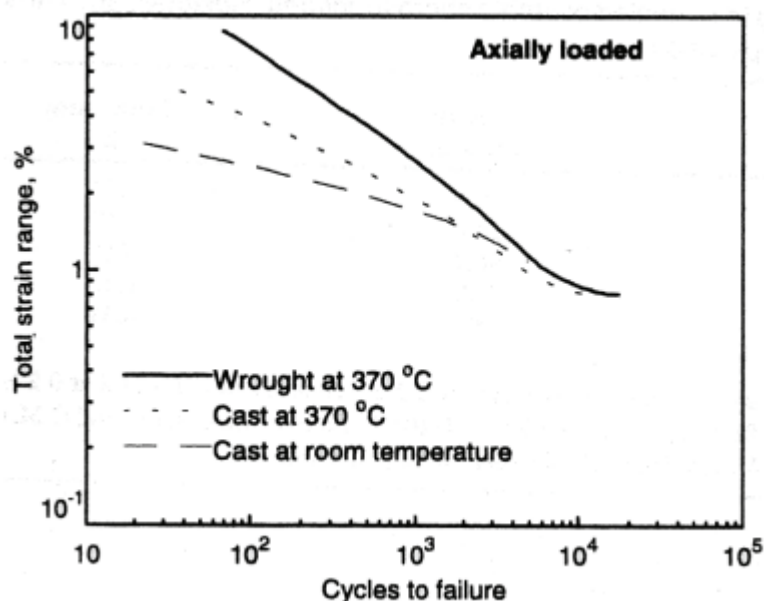


Figure 2-4 A side-by-side overview of low-cycle fatigue (LCF) performance comparing cast and wrought Ti6Al4V (M. J. Donachie, 2000).

2.1.3.4 Fatigue Crack Growth

Fatigue crack growth (FCG) takes on particular importance during the second phase of fatigue failure, as it represents how much remaining fatigue life is left once a crack is already present, but before the material finally fractures (Dieter & Bacon, 1988). Researchers often examine

this by using tensile specimens that already have a crack, plotting the FCG rate (da/dN) against the stress intensity range at the crack tip (ΔK). Evidence suggests that the microstructure heavily influences FCG in titanium alloys—for instance, in Ti6Al4V, a lamellar arrangement tends to slow the propagation of fatigue cracks compared to an equiaxed (globular) structure under equivalent loading conditions ($R = \sigma_{\min}$ to $\sigma_{\max}$). Consequently, cast titanium alloys containing a coarse lamellar structure demonstrate greater resistance to FCG compared to wrought variants (M. J. Donachie, 2000; Leyens & Peters, 2006; Nastac et al., 2006). Among the microstructural features that shape FCG behaviour, the α colony size plays the most pivotal role. A larger α colony size generally offers better defence against fatigue crack propagation (Leyens & Peters, 2006). In addition, FCG rates show a high level of sensitivity to surrounding conditions such as air, hydrogen, or a vacuum. It has been observed that FCG progresses at a faster pace in air than in a vacuum across different microstructures. However, lamellar structures experience a more pronounced environmental effect due to their extended slip lengths, which promote quicker crack growth (Lütjering, et al., 2000; Schroeder et al., 2001).

2.1.4 Texture Formation in Titanium Alloys

Crystallographic texture essentially describes how certain crystallographic orientations are favoured in a polycrystalline material. In the case of Ti alloys, examining this texture is quite significant for several reasons. Since texture usually results from deformation during both primary and secondary processing, it can be a useful indicator of an unknown thermo-mechanical history of a Ti alloy (Pilchak, 2009). Moreover, because the evolution of crystallographic texture in Ti alloys is closely tied to their solidification route, analysing texture provides a solid foundation for understanding the microstructure in question (S. S. Al-Bermani et al., 2010; Knipling & Fonda, 2011). Beyond that, research has indicated that the grain-level crystallographic orientation in Ti alloys influences their fracture behaviour under various conditions, which in turn affects their tensile and fatigue characteristics (Peters et al., 1984; Pilchak et al., 2012; Pilchak & Williams, 2011).

To support the discussion of the findings in this study, this section takes a closer look at how texture develops during conventional titanium alloy processing and how plastic deformation interacts with crystallographic texture in these alloys. The underlying principles of crystallographic texture formation in metals, including Ti alloys, are well established (Kocks et al., 2000). When polycrystalline metals are strained, each grain deforms through specific slip or twinning systems, and this external loading causes atoms in the crystal lattice to shift, leading to a rotation of the lattice relative to its initial state. The resulting grain orientations are termed equilibrium orientations. Although it can be complicated to predict these final equilibrium orientations in a polycrystalline metal, certain established models have shown that they can be derived from a few core theoretical frameworks (Beausir et al., 2007). In particular, given the original orientation of a grain, the ultimate equilibrium orientation often depends on the symmetry of the crystal phase of the polycrystalline material. Grains tend to deform in a way that maximizes resolved shear stress on the slip system with the lowest critical resolved shear stress (Beausir et al., 2007). In $\alpha+\beta$ Ti alloys specifically, the α phase typically dominates the microstructure and features three main slip systems, as illustrated in Figure 2-5.

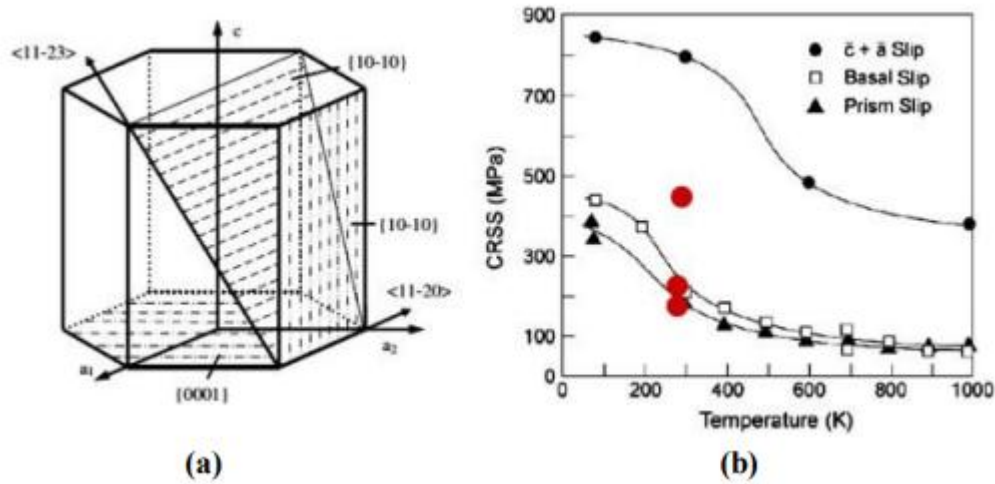


Figure 2-5 Illustrative diagram showing (a) the slip systems in the α phase and (b) their corresponding critical resolved shear stress (CRSS) (D. Banerjee & Williams, 2013).

The slip system that has the lowest critical resolved shear stress (CRSS) is the prismatic $\langle a \rangle$ slip $\{10\bar{1}0\}\langle 11\bar{2}0 \rangle$. As illustrated in Figure 2-5, this is followed by the basal $\langle a \rangle$ slip $\{0001\}\langle 11\bar{2}0 \rangle$, and then the pyramidal $\langle a+c \rangle$ slip $\{11\bar{2}2\}\langle 11\bar{2}3 \rangle$, which is roughly two to five times harder to activate than the other two slip systems (Lütjering & Williams, 2007). Because there is only a restricted set of slip systems available to accommodate deformation, mechanical processing of $\alpha+\beta$ Ti alloys can generate a pronounced texture in the α phase, and thereby in the final material. In practical terms, the α texture of a Ti alloy component is mainly influenced by these key processing stages:

- the solidification step during ingot/cast fabrication (solidification texture)
- the final deformation step in the $\alpha+\beta$ or β phase range (stage II) (deformation texture)
- the cooling rate after recrystallization or annealing (stage III) (transformation texture)

When the β phase transforms into the α phase, it follows the Burgers crystallographic orientation relationship (BOR), which stipulates that:

$$\begin{aligned} \{110\}_{\beta} &\parallel \{0001\}_{\alpha} \\ \langle 111 \rangle_{\beta} &\parallel \langle 11\bar{2}0 \rangle_{\alpha} \end{aligned}$$

In simpler terms, once the phase transformation takes place, the $\{0001\}$ basal planes of the α phase become parallel to the $\{110\}$ planes of the β phase, and the close-packed direction $\langle 11\bar{2}0 \rangle$ lines up with the $\langle 111 \rangle$ direction described in (Donachie, 2000). Due to the presence of six non-parallel $\{110\}$ planes and two non-parallel $\langle 111 \rangle$ directions, up to 12 distinct crystal orientations (often called 12 α variants) can form from a single β grain. Consequently, any preferred orientation established in the β phase during solidification or mechanical deformation restricts the number of α variants that can emerge. During initial fabrication, titanium ingots display a solidification microstructure that may comprise either columnar β grains (originating from the chill zones near water-cooled crucibles) or equiaxed β grains. In cases involving

columnar β grains, it has been observed that the β phase develops a $\langle 100 \rangle$ fiber texture following $\langle 100 \rangle$ the growth direction of these grains (D. Banerjee & Williams, 2013). Conversely, when the microstructure consists of equiaxed β grains, the β texture is generally weak or random (D. Banerjee & Williams, 2013). On the other hand, if the β phase shows a pronounced $\langle 100 \rangle$ fiber texture, then regions featuring α textures of varying intensities can form (D. Banerjee & Williams, 2013).

A considerable amount of work has gone into achieving Ti alloys that present a uniform and favourable α texture, focusing on how deformation texture in Ti alloys develops (Semiatin et al., 1997; Gey et al., 1996; Gey et al., 1997; Gey et al., 2002; Zaefferer et al., 2003; Lütjering & Williams, 2007; Salem et al., 2008; Obasi et al., 2012). Researchers have established that carrying out mechanical deformation at relatively low temperatures within the $\alpha+\beta$ phase field (often around 800 °C) directly influences the preferred texture in the α phase (Lütjering & Williams, 2007). The resulting texture symmetry is highly dependent on the chosen deformation path. For instance, during one-directional rolling, the material typically develops what's known as a basal/transverse (B/T) texture, as illustrated in Figure 2-6.

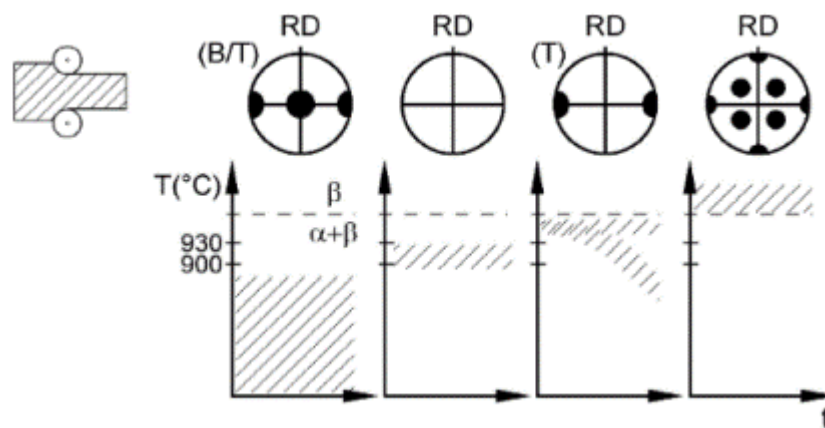


Figure 2-6 Visual representations of deformation textures in $\alpha+\beta$ Ti alloys shown through basal pole figures (Lütjering & Williams, 2007).

As the temperature for the deformation process goes up (which also increases the β -phase volume fraction), the (B/T) texture gradually disappears since the deformation is mainly taking place in the β phase (Figure 2-6). Nevertheless, it remains feasible to produce Ti alloys exhibiting moderate to strong α texture. For instance, when unidirectional rolling is performed below the β transus temperature, a so-called transverse (T) texture can preferentially develop (Figure 2-6). The interplay between the deformed β and the subsequent α texture is far from straightforward and is not yet fully clarified (Sargent et al., 2012). It is established that, at temperatures close to or higher than the β transus, mechanical deformation leads to a favoured texture in the β phase. In that context, experimental observations suggest that the intensity of the resulting α texture will hinge on both the deformation path and the cooling rate. The proposed rationale is that β grains undergoing the most pronounced mechanical deformation serve as ideal nucleation sites for the α phase (Sargent et al., 2012). The crystal slip activity within these grains entails high dislocation density and elevated stored elastic energy, which in

turn prompts α nucleation upon cooling. According to these findings, substantial slip on $\{110\}\langle 111 \rangle$ and $\{112\}\langle 111 \rangle$ systems can encourage plates to form in specific variants (Gey & Humbert, 2003). The cooling rate applied during the $\beta \rightarrow \alpha$ transformation then determines the size of the α colony born from each α variant, thereby impacting the resulting α texture strength.

A number of investigations have examined the influence of the cooling rate on α variant selection during the $\beta \rightarrow \alpha$ transformation (often referred to as α transformation texture) when there is no prior mechanical deformation (Gey & Humbert, 2003; D. He et al., 2012; Karthikeyan et al., 2010; Sargent et al., 2012; Semiati et al., 2013). In spite of there being 12 potential solutions during the $\beta \rightarrow \alpha$ transformation, a slower cooling rate does not lead to an even spread of these 12 variants in the specimen. Several explanations have been advanced to elucidate how the cooling rate during $\beta \rightarrow \alpha$ influences the favoured variant selection (D. Banerjee & Williams, 2013). In situations where neighbouring β grains exhibit parallel $\{110\}$ planes, it is believed that particular variants whose $[0001]$ directions are nearly parallel on both sides of the boundary tend to dominate when cooling rates are sufficiently slow (Bhattacharyya et al., 2003; Stanford & Bate, 2004a). In other words, any variant forming along a grain boundary should adhere to the Burgers orientation relationship with its original β grain as well as with adjacent β grains. Interestingly, a similar requirement has been noted in micro-alloyed steels during ferrite-to-austenite transformations (Lischewski & Gottstein, 2011). When cooling is slow, α lath colonies are more likely to continue growing in the orientation of the selected variant, thereby minimizing the energy cost of nucleating α phases in different orientations.

However, it is not unusual in Ti alloys to observe α colonies emerging from within the prior β grain (as opposed to the grain boundary), suggesting that the above mechanism may not fully explain the phenomenon (Lütjering & Williams, 2007). Furthermore, newer findings indicate that the secondary α texture formed after annealing and cooling from the $\alpha + \beta$ phase region of Ti6Al4V aligns with the primary α texture (Sargent et al., 2012). Consequently, the core principles of variant selection have been investigated in terms of the stresses and strains involved in the $\beta \rightarrow \alpha$ transformation (Sargent et al., 2012). It has been suggested that local stresses build up during cooling due to the difference in thermal expansion coefficients of each phase. Thus, it was proposed that, to reduce the elastic strain energy of the β phases, the orientation of the parent β phase should be arranged accordingly (Humbert et al., 2006).

Studies have also found that repeatedly β -annealing and cooling Ti alloys to room temperature gives rise to β grains sharing the exact same texture (Semiati et al., 2013). This so-called β “memory effect” may be driven by the need to minimize strain energy during the $\alpha \rightarrow \beta$ transformation. Similarly, research has shown that α texture remains stable through repeated annealing cycles (a phenomenon known as texture inheritance), highlighting that the same energy-minimizing principle applies during repeated $\alpha \rightarrow \beta \rightarrow \alpha$ transformations (Lonardelli et al., 2007; G. C. Obasi, Biroscu, Leo Prakash, et al., 2012). Even so, a recent grain-by-grain examination of the orientation relationship between α and β phases revealed instances where the energy-minimization rule was not followed (Sargent et al., 2012). It was discovered that some individual grains adopt so-called “non-favourable” orientations, stemming from

transformations that do not yield the lowest possible strain. Still, the average strain over several adjacent β grains was substantially lower than that in a scenario of purely random transformation (i.e., without variant selection). Thus, it was concluded that strain energy minimization should be considered on a scale involving multiple neighbouring grains, rather than individual grains. When the cooling rate linked to $\beta \rightarrow \alpha$ increases, α colonies become smaller and the full set of 12 possible variants is distributed more uniformly (D. Banerjee & Williams, 2013; D. He et al., 2012).

Triangular formations of certain α variants are frequently seen within the prior β grains, and it is hard to accept that these groupings happen purely by chance out of the 12 α variants. Their origin remains somewhat elusive (D. Banerjee & Williams, 2013). The most accepted explanation at the moment is based on the self-accommodation concept of neighbouring variants (S. C. Wang et al., 2003). Various mathematical investigations suggest that certain variant groupings are favoured over others to reduce the strain from the phase change (D. Banerjee & Williams, 2013). Two types of clusters, each made up of three variants in a triangular arrangement, have been identified as the most energetically favourable. These clusters consist of α variants misoriented in the specific manner detailed by S. C. Wang et al., 2003. Exploring the texture formation in $\alpha+\beta$ Ti alloys, such as Ti6Al4V, is particularly complex because only minimal β phase remains at room temperature, making it difficult to directly measure β texture with confidence. Several references show attempts to derive β texture from α texture measurements (Gey & Humbert, 2003; Glavicic, Kobryn, Bieler, et al., 2003). In practice, the β phase texture can be back-calculated by first determining α variant orientations—often via EBSD—and then applying the Burgers orientation relationship to infer the β texture.

2.2 Ti6Al4V and its Microstructure

Within the $\alpha+\beta$ group of titanium alloys, Ti6Al4V stands out as the most extensively utilised alloy composition. This alloy is engineered principally for high strength across a range of low to moderate temperatures. It possesses remarkable specific strength, remains stable at temperatures reaching up to 400°C, and offers excellent corrosion resistance (Leyens & Peters, 2006; X. Li et al., 2009; Lütjering & Williams, 2003). However, its cost remains a significant barrier unless the properties mentioned earlier are essential.

The composition of Ti6Al4V varies widely based on its intended use. The oxygen concentration in the alloy can range from 0.08% to over 0.2% by weight, while nitrogen levels can be regulated up to 0.05%. The alloy might contain up to 6.75 wt% aluminium and up to 4.5 wt% vanadium. Increasing the compositions of certain elements, especially oxygen and nitrogen, tends to enhance the strength of the alloy but at the cost of reducing its ductility, fracture toughness, resistance to stress corrosion, and ability to withstand crack propagation (Welsch et al., 1993). There exist also ELI (extra-low interstitial) and Pd (about 0.2 wt%) grades of Ti6Al4V, known for their superior damage tolerance and corrosion resistance. The range of microstructures that Ti6Al4V can develop is significantly influenced by its heat treatment process and the amounts of interstitial elements present. Consequently, the alloy

chemical composition and its thermal treatment history play a pivotal role in determining its mechanical characteristics (Polmear et al., 2017).

Ti6Al4V is available in various forms including wrought, cast, and powder metallurgy (P/M), with wrought forms making up over 95% of its presence in the market (Welsch et al., 1993). The interstitial contents and thermal-mechanical processing of the alloy dictate the specific properties of the aforementioned forms. The aerospace sector extensively employs all forms of wrought products, utilizing forgings to create different attachment fittings, while sheets and plates are utilised to form a variety of clips, brackets, skins, bulkheads, and more. Ti6Al4V, maintaining the same chemical composition as its wrought counterparts, exhibits superior casting qualities. Nonetheless, the highly reactive nature of titanium when the alloy is in the molten state necessitates advanced casting techniques, limiting the expansion of titanium foundries (Welsch et al., 1993). Generally, cast versions of Ti6Al4V tend to have slightly lesser mechanical and fatigue properties compared to wrought products, yet their fracture toughness, stress corrosion cracking (SCC) resistance, and resistance to crack propagation are comparable with annealed wrought Ti6Al4V (Pederson, 2002). Beyond wrought and cast forms, P/M products are developed into near-net shapes, with a significant focus on Ti6Al4V due to its widespread use and extensive comparative data (Welsch et al., 1993). The approaches to titanium P/M primarily include the blended element technique and the pre-alloyed method. The processing of titanium alloys consists of a sequence of four key processes: homogenization, deformation, recrystallization, and aging (see Figure 2-7), each influencing the final microstructure of the alloy in distinct ways (D. Banerjee & Williams, 2013; Lütjering & Williams, 2003). The morphology and presence of β grains, especially at room or operational temperatures, play a significant role in defining the ultimate characteristics of the alloy. However, it is the morphology of β -titanium at temperatures exceeding normal service temperatures, particularly beyond the $T_{transus}^{\alpha/\beta}$ temperature—where the α phase becomes unstable—that attracts interest. The morphology of β -titanium in these super-transus conditions critically affects how the α -titanium phase evolves as it cools from the temperatures used during processing or shaping.

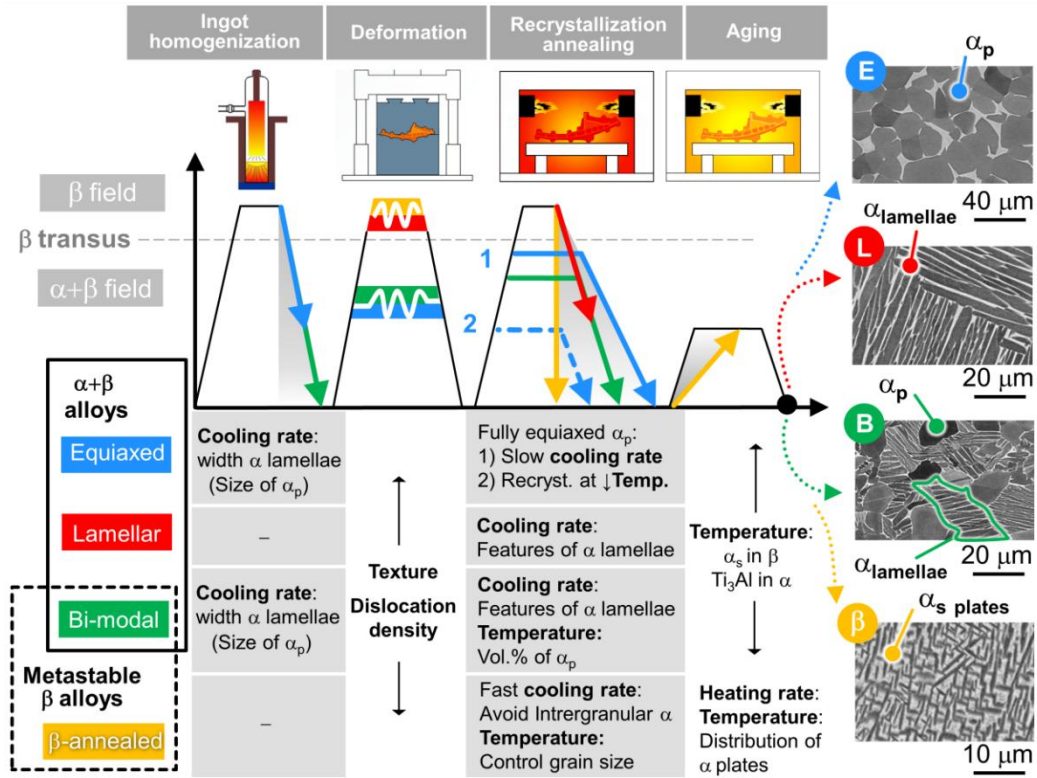


Figure 2-7 Processing paths for conventional microstructures in α+β and metastable β titanium alloys, equiaxed, lamellar, bi-modal and β-annealed. It highlights key parameters at each processing stage and showcases the corresponding microstructures through SEM images for each specified condition (Vila, 2015).

Equiaxed and lamellar microstructures represent the most illustrative example of different phase arrangements in titanium alloys. The first one consists in primary α (α_p) grains embedded in a β matrix. It can be obtained after deformation through two different ways: upon slow cooling after homogenization from temperatures slightly below $T_{transus}^{\alpha/\beta}$ temperature, or via recrystallization of α at moderate temperatures (see Fig. 2.4). On the other hand, the lamellar microstructure is composed of packets of α lamellae that grow via β → α transformation within β grains during cooling from temperatures above $T_{transus}^{\alpha/\beta}$ temperature (see Figure 2-7). In this case, the deformation step can be carried out either in β or α+β field. Bi-modal microstructures are a combination of equiaxed and lamellar grains: colonies of α lamellae distributed within β grains coexist with α primary grains located at the triple points of β grain boundaries. This microstructure is basically the result of a recrystallization process in α+β field, where the degree of deformation, and the cooling rates during homogenization and recrystallization are important to control the size and width of α_p and α lamellae, respectively (see Figure 2-7). Precipitation of secondary α (α_s) plates in β grains is normally induced during the final aging treatment of α+β alloys due to its positive strengthening effect (Figure 2-7) (Leyens & Peters, 2006; Lütjering & Williams., 2003).

2.2.1 Phase Transformation

In α+β alloys like Ti6Al4V, the phase transformation from β→α phase occurs as the material cools down through the $T_{transus}^{\alpha/\beta}$ temperature. At ambient temperature, this transformation from

$\beta \rightarrow \alpha$ phase is not entirely complete, leaving around 10% of the β phase by volume in the final microstructure. For a standard Ti6Al4V alloy, this critical transus temperature is around 1273K (1000°C), and this temperature is significantly influenced by the presence of interstitial impurities, notably oxygen (Malinov et al., 2001). The impact of vanadium content on phase stability within a Ti6Al4V alloy is depicted in a pseudo binary phase diagram, as illustrated in Figure 2-8.

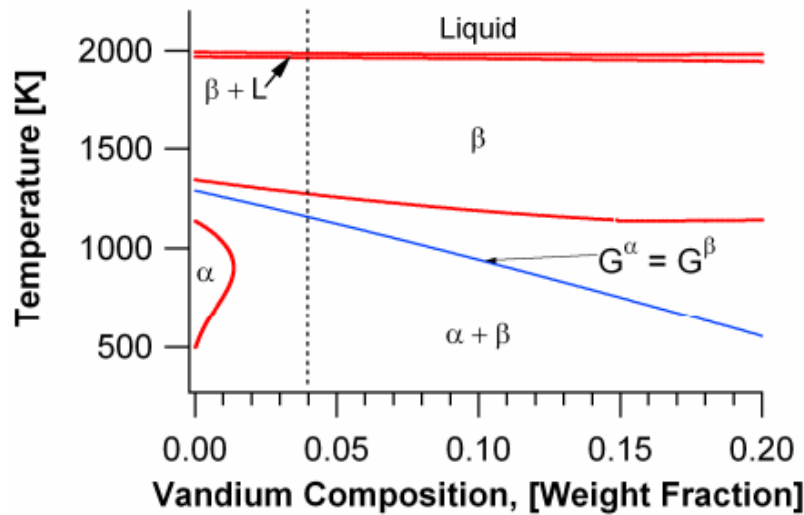


Figure 2-8 Pseudo-binary phase diagram showing the phase variation with respect to vanadium composition, calculated with ThermoCalc software. The alloy composition is fixed as Ti-6Al-3.99V-0.25Fe-0.203O-0.021C-0.013N (S. Kelly, 2004).

During the cooling down through the $T_{transus}^{\alpha/\beta}$ temperature, the β phase in Ti6Al4V can undergo transformation into multiple α phase morphologies, including diffusion-controlled allotriomorphic and Widmanstätten alpha, massive (α_m), and martensitic (α') alpha. Table 2-1 contains the recently studied typical cooling rates for these transformation products (Ahmed & Rack, 1998).

Table 2-1 Typical transformation products for $\beta \rightarrow \alpha + \beta$ and associated cooling rate and start temperatures.

Transformation Product	Cooling Rate (K/s)	Start Temperature (°C)
Allotriomorphic (α_{GB})	CR < 20	1243-1273K
Widmanstätten (α_W)	CR < 20	~1173K [47]; ~1223K [48]
Massive (α_m)	20 < CR < 410	1243-1273K
Martensitic (α')	CR > 410	$M_s = 848K$

Figure 2-9 graphically illustrates the common phase transformations that occur during a thermal cycle of heating and cooling, where the peak temperature exceeds the $T_{transus}^{\alpha/\beta}$ temperature. In the figure, the path labelled AB depicts the heating process exceeding the $T_{transus}^{\alpha/\beta}$ temperature, resulting in the complete dissolution of the α phase. The paths CD and CE represent the transformation of β phase into non-equilibrium phases martensitic α' and massive α_m during rapid cooling. Meanwhile, the path labelled CF indicates a diffusional transformation

from β to a dual-phase structure composed of primary-alpha (α_p) and β phases. Heat treatment that follows the A-BC-F temperature-time trajectory is known as "primary" treatments, resulting in the formation of primary-alpha microstructures.

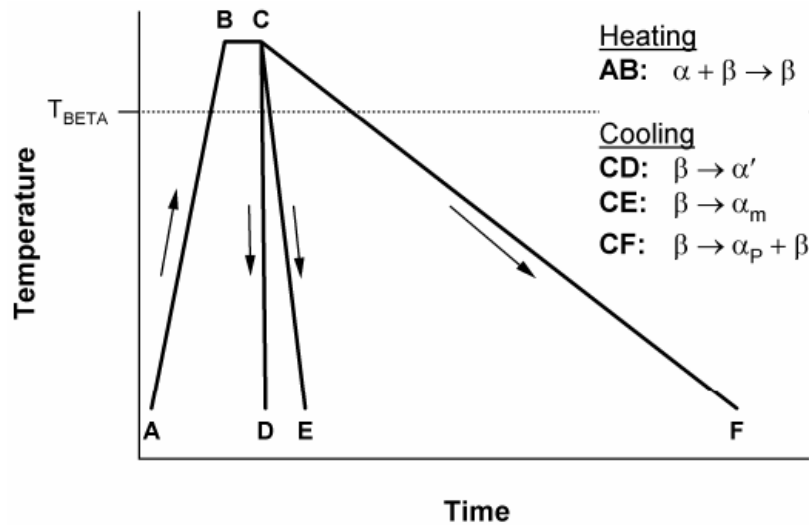


Figure 2-9 Diagram illustrating the primary heat treatment process above the β -transus, showing the full transition of α into β (AB), and subsequent cooling at varying rates resulting in the formation of martensitic α' (CD), massive α (α_m) (CE) and primary- α (α_p) and retained β phase (CF) (S. Kelly, 2004).

Figure 2-10 graphically demonstrates the reactions that occur during a secondary heat treatment cycle, where both heating and cooling take place beneath the $T_{transus}^{\alpha/\beta}$ temperature. In this visual illustration, GH represents the phase where primary-alpha dissolves, leading to the initial alpha phase (in this case α_p) dissolving into β , creating a mixture of α_p and β . As the cooling progresses through IJ path, areas of newly formed β break down into secondary- α (α_s) phase, resulting in a composition that includes retained β along with primary- and secondary- α phases. Primary- α phase emerges when cooling from temperatures just over the $T_{transus}^{\alpha/\beta}$ temperature, whereas secondary- α phase develops through heating and cooling within the dual phase area.

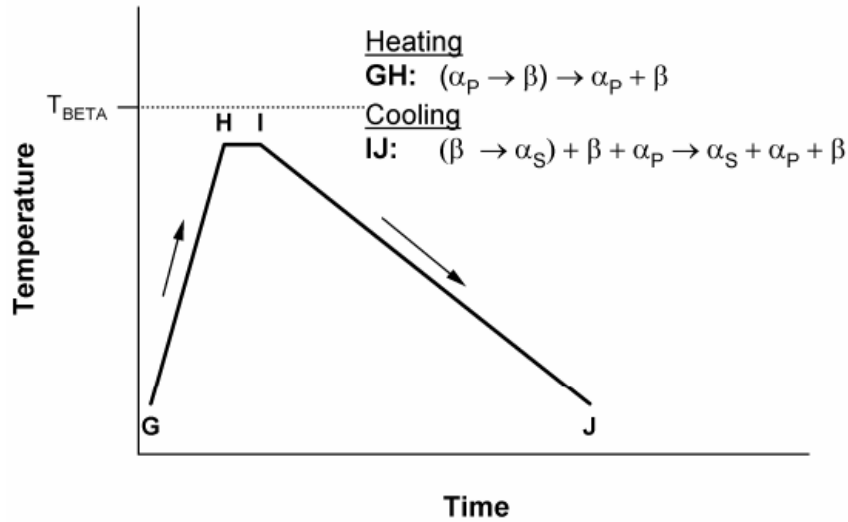


Figure 2-10 Illustrative depiction of a secondary heat treatment process limited to temperatures below the beta transus, showcasing the dissolution of primary-alpha (α_p) into β upon heating (GH), followed by the formation of secondary-alpha (α_s) from the dissolved α_p during cooling (IJ). The ultimate microstructure is a mixture of α_p , α_s , and β (S. Kelly, 2004).

2.2.2 Crystallography of $\beta \rightarrow \alpha + \beta$ Reaction

As $\alpha + \beta$ titanium alloys are solidified from high temperatures, a range of phase changes can occur, influenced by the alloy's specific chemical composition and how quickly it cools. These transformations can include martensitic transformation, interface-diffusion controlled massive transformation, and transformation governed by diffusion that leads to nucleation and growth (Y. Sun, 2016). Often, the BCC β -phase transforms into the HCP α -phase, obeying the classic Burgers orientation relationship that shows the crystallographic orientation relationship between α and β as (L. Murr et al., 2012; Burgers 1934; H. Tang et al., 2015):

$$\begin{aligned} \{110\}_{\beta} \parallel \{0001\}_{\alpha} \\ \langle 111 \rangle_{\beta} \parallel \langle 11\bar{2}0 \rangle_{\alpha} \end{aligned} \quad 2.1$$

Transformations similar to those described by Burgers can result in up to 12 unique α orientations or variants from a singular β orientation (M. Qian et al., 2016) as can be seen from Figure 2-11. Conversely, a single α crystal can lead to six different β orientations. Theoretically, during an $\alpha \rightarrow \beta \rightarrow \alpha$ phase transformation, there are a total of seventy-two possible Burgers orientation relationships (Shang et al., 2002). However, in practice, this extensive variety is rarely observed due to the process of variant selection. Variant selection has been observed in transformations that are both martensitic in nature and transformations controlled by diffusion (G. Obasi et al., 2012; Stanford & Bate, 2004; Y. Wang & Huang, 2003).

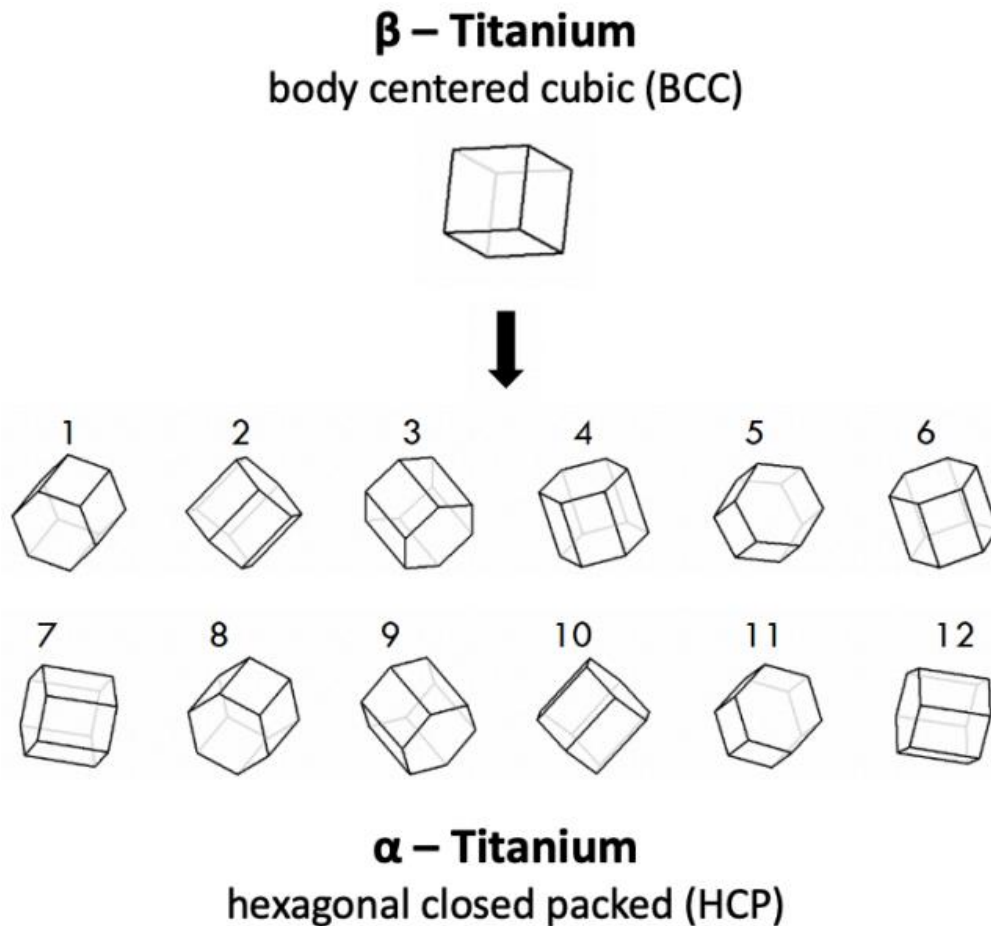


Figure 2-11 Schematic of 12 distinct α orientations or variants from a single β grain (M. Shao, 2021).

2.2.3 Diffusion Controlled $\beta \rightarrow \alpha + \beta$ Reaction

The formation of allotriomorphic grain boundary alpha (α_{GB}), colony primary alpha (α_P), and Widmanstätten α inside the previously existing β grains results from transformations controlled by diffusion, which necessitates the partitioning of solute components.

2.2.3.1 Allotriomorphic Grain Boundary α ($\beta \rightarrow \alpha_{GB}$)

The Continuous Cooling Transformation (CCT) diagram in Figure 2-12 visually represents the series of nucleation and growth processes that develop as the material cools down at a relatively slow rate through the $T_{transus}^{\alpha/\beta}$ temperature. This CCT diagram highlights the initial phases of transformation for both allotriomorphic (or "grain boundary") α and intragranular α . When the alloy cools through the $T_{transus}^{\alpha/\beta}$ temperature, allotriomorphic or "grain boundary" α is the first phase to form, due to its positioning along the β grain boundaries. This is because of the presence of the grain boundaries that always act as an effective nucleation site. Although this is the initial α phase to form during cooling through the $T_{transus}^{\alpha/\beta}$ temperature, it is referred to not as primary- α but as grain boundary α (α_{GB}). Over time, the β grain boundaries will become fully filled with grain boundary α phase, which can occur in either a continuous or discontinuous manner—the latter being a result of faster cooling or a higher content of β stabilizer alloying element in the alloy (R. Banerjee, Bhattacharyya, et al., n.d.). Grain boundary

α typically displays a Burgers orientation relationship with at least one of the β grains from which it originates (Bhattacharyya et al., 2003; Ohmori et al., 1994; Stanford & Bate., 2004).

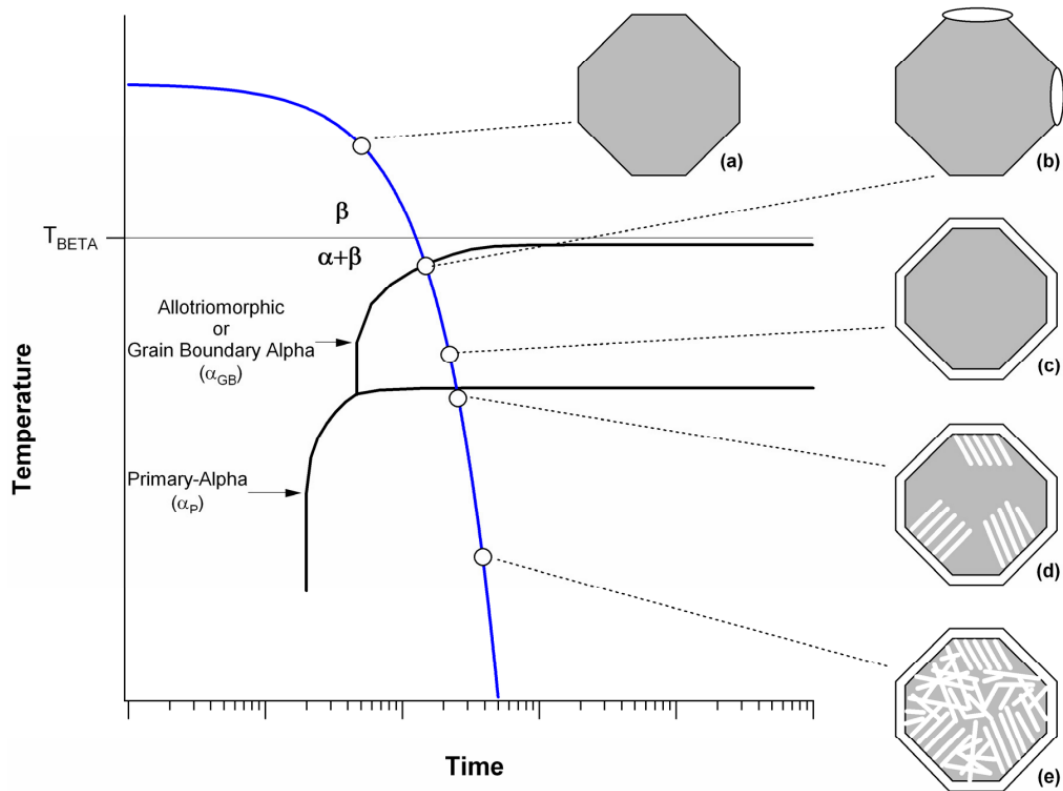


Figure 2-12 Diagram depicting the progression of diffusion-controlled phase changes that take place as Ti6Al4V alloy cools continuously through the $T_{transus}^{\alpha/\beta}$ temperature, with initial transformation curves for both allotriomorphic (grain boundary α) and intragranular α presented. (a) illustrates a single β grain in grey. (b) demonstrates that the initial α to form is allotriomorphic Widmanstätten α at the β grain boundaries. (c) shows the growth of α phase along the β grain boundaries. (d) highlights the beginning of nucleation and growth of primary- α at the grain boundary α in the form of primary- α sideplate colonies, and finally, (e) with further undercooling, primary- α starts to nucleate within the remaining β matrix, adopting a basketweave pattern (M. Donachie, 2000; S. Kelly, 2004).

Although not depicted in Figure 2-12, massive and martensitic transformations might still occur during the cooling phase of a secondary heat treatment, given that the peak temperatures exceed the T_0 temperature and cooling is rapid enough. The T_0 temperature is the point at which α and β phases share equal Gibbs free energy. Below the T_0 temperature, transforming to either massive or martensitic α phase reduces the free energy of alloy.

2.2.3.2 Primary- α (α_P) Colony Morphology ($\beta \rightarrow$ Colony α_P)

As the material experiences further undercooling, primary- α sideplates or colonies start to emerge from the grain boundary α phase (as shown in Figure 2-12 (d)), growing into the original β grain where a coherent Burgers orientation relationship is maintained; that is, these primary- α colonies can be seen as a type of Widmanstätten α phase (Ohmori et al., 1994). These individual α grains are characterized by their elongated shape (not equiaxed) and typically group together into colonies, where multiple α phase plates align parallel to each other, driven

by the favourable orientations at the β grain boundary. Primary- α plate colonies start to form and grow within the β grains until they encounter other α plates emerging from the other side of the grain, potentially representing different Burgers orientation relationship variants. When these α phase plates form from the grain boundary α interface, they often maintain a low angle grain boundary (Furuhashi et al., 1996) and align according to the Burgers orientation relationship with the prior β phase. This arrangement leads to a diffusional transformation-induced microstructure characterized by parallel alpha plates separated by the remaining β matrix, known as a “lamellar microstructure” (M. Donachie, 2000; Leyens & Peters, 2006). Illustrations of the α_{GB} and α_P colony structures are provided in the SEM – BSE micrograph in Figure 2-13. As the cooling rate increases, the individual α plates become narrower, the overall colony size decreases, and the number of α plates within each colony is reduced (Ahmed & Rack, 1998; M. Donachie, 2000).

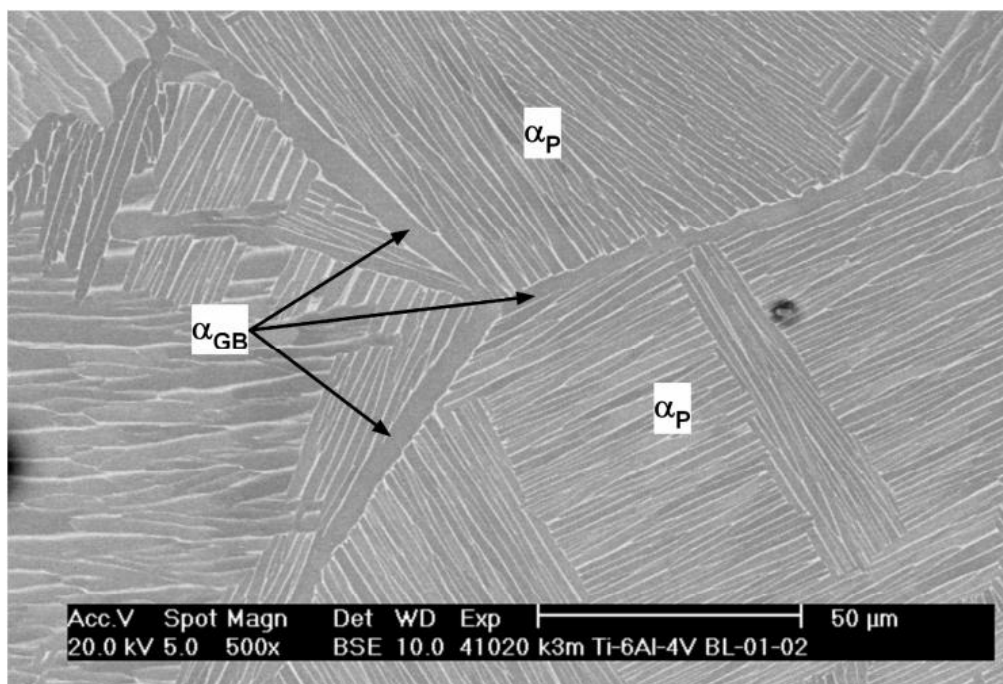


Figure 2-13 BSE micrograph depicting the morphologies of grain boundary alpha (α_{GB}) and primary-alpha (α_P) colonies, which arise through diffusion-controlled transformation as the material cools through the beta transus. The β phase appears in white contrast, while the α phase appears in grey contrast (A. Antonysamy, 2012).

2.2.3.3 Basketweave Primary- α (α_P) Morphology ($\beta \rightarrow$ Widmanstätten α):

The final Widmanstätten α structures emerge within the residual β matrix in a pseudo-random manner, selecting one of the twelve possible crystallographic variants. This is due to the high driving force for α phase formation at greater degrees of undercooling, which promotes the α grains to initiate within the remaining β . This particular α phase morphology is known as the primary-basketweave α . An illustration of α_{GB} , α_P colonies, and the basketweave pattern can be seen in Figure 2.7. The likelihood of developing a basketweave structure is increased by the rate of cooling. In the case of slow cooling rates, Widmanstätten sideplates grow to consume the available β phase, preventing the formation of high undercooling necessary for basketweave pattern to form (S. Kelly, 2004). Additionally, β grains of smaller size are more prone to

developing colony α rather than basketweave structures. Furthermore, alloys that are significantly stabilized by β stabilizing alloying elements are more prone to basketweave formation, as these compositions require less undercooling to initiate the process (S. Kelly, 2004; Leyens & Peters, 2006).

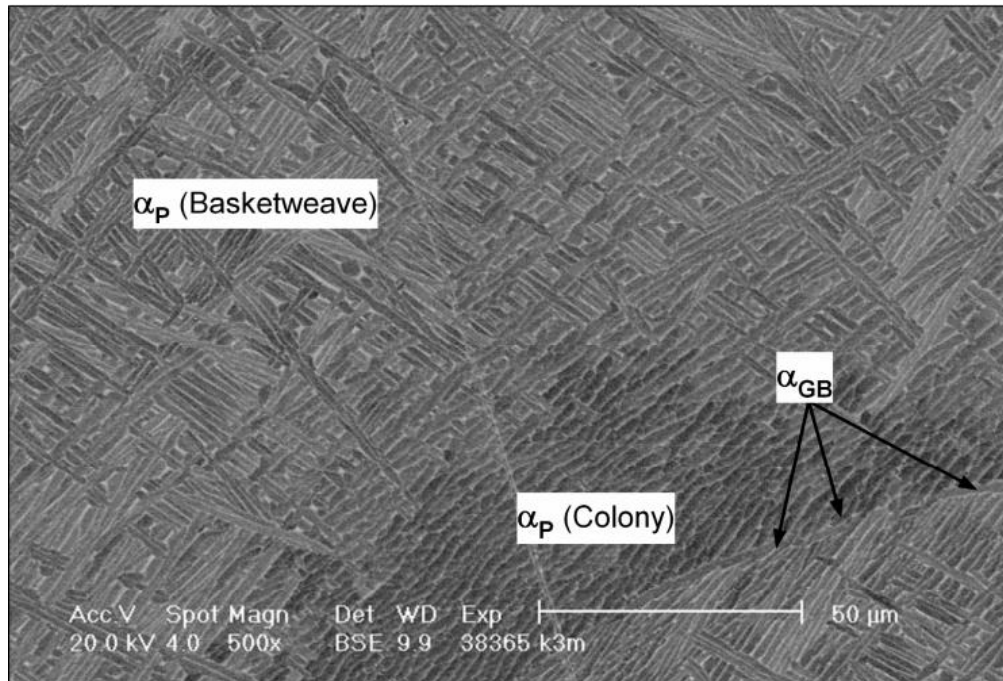


Figure 2-14 BSE micrograph illustrating the morphologies of grain boundary α (α_{GB}) and primary- α (α_P) in both colony and basketweave forms, developed through diffusion-controlled transformation during cooling past the β transus temperature. In this image, β is represented by the white contrast, while α is distinguished by the darker contrast (A. Antonysamy, 2012).

2.2.4 Diffusionless Martensitic Transformation ($\beta \rightarrow \alpha'$)

Though originally used to define the hard, needle-like phase that emerges in steels upon quenching, the term “martensite” and the process of martensitic transformation are observed across a broad spectrum of metals and alloys. The transformation of a parent phase into martensite represents a diffusionless change, involving the coordinated shift of atoms to create a martensite structure that retains the same chemical composition as the original phase (S. Al-Bermani, 2011; Nishiyama, 2012). In the context of nucleation and growth process, the martensitic transformation faces a significant obstacle in initiating nucleation stage due to a high energy barrier, while the obstacle for growth stage is nearly zero. This barrier to nucleation demands significant undercooling below the equilibrium transformation temperature. On the other hand, the minimal barrier to growth allows for the rapid expansion of martensite grains, with speeds that can near the speed of sound (S. Al-Bermani, 2011). The martensitic α' appears usually plate shaped or more accurately described its shape geometrically as disk-shaped. The hexagonal form of martensite, known as α' , manifests in two distinct patterns: the dense, “massive” martensite (also referred to as lath or packet martensite) and the finer, “acicular” martensite (Williams, 2013). Massive martensite typically forms in pure titanium, alloys with minimal solute, or those with a high martensitic transformation temperature, whereas “acicular” martensite is found in alloys with a higher solute concentration, leading to a lower martensite

transformation temperature (Leyens & Peters, 2006). The $\beta \rightarrow \alpha'$ transformation adheres to the Burgers orientation relationship, similar to the nucleation and growth of the equilibrium α phase, with specified orientations for both the β and α' phases and designated habit planes (S. Kelly, 2004). Martensitic plates often exhibit a high density of dislocations and occasionally twins. HCP α' martensite, rich in β stabilizers, breaks down into $\alpha + \beta$ through the precipitation of β particles at dislocations or along plate boundaries upon annealing in the $\alpha + \beta$ phase region (M. Donachie, 2000). As the solute content increases, the hexagonal structure distorts, transitioning from hexagonal to orthorhombic symmetry, referred to as α'' (Williams, 2013). This orthorhombic martensite, upon early annealing stages in the $\alpha + \beta$ phase field, undergoes spinodal decomposition, creating a modulated microstructure of solute lean and rich α'' regions, eventually leading to the precipitation of the β phase and forming a mixed $\alpha + \beta$ structure (Flower et al., 1982). The extent to which α' martensite forms is directly related to the cooling rate, as detailed in Figure 2-15. When the cooling rate exceeds 410°C/s , a completely martensitic α' structure is achieved. Conversely, cooling rates that fall between 410°C/s and 20°C/s result in an incomplete formation of the α' structure.

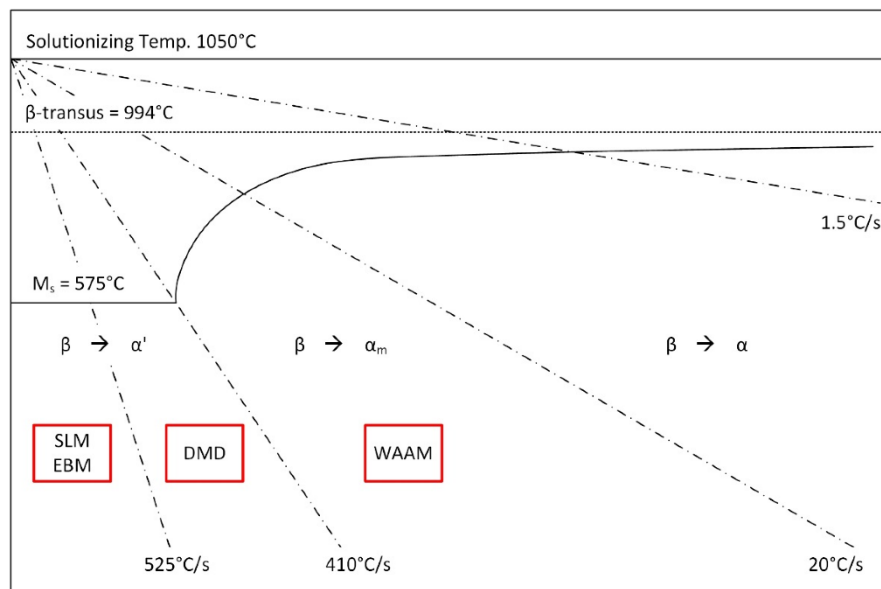


Figure 2-15 Diagram depicting the continuous cooling of Ti6Al4V, solution-treated at 1050°C for 30 minutes and quenched with the Jominy end quench test, illustrating the correlation with cooling rates encountered across four additive manufacturing processes (Cottam et al., 2019).

2.3 Boron Additions to Titanium Alloys

As highlighted in previous sections, despite widespread availability and appealing properties of titanium, its usage remains limited (Welsch et al., 1993). The primary reason for this limitation is the high cost associated with extraction, melting, and both primary and secondary processing (Imam et al., 2010). Figure 2-16 illustrates a typical processing schedule for titanium, including a comprehensive cost analysis for each step (Roskill Information Services Limited, 2001). The primary contributor to these high costs ($\sim 60\%$ of the total) is the energy-intensive nature of melting and fabrication processes. Ongoing research aims to develop innovative methods to address this issue (Mitchell, 1998). Another significant cost factor is

primary wrought processing, which involves "ingot breakdown" through β working and secondary processing through $(\alpha+\beta)$ working. As depicted in Figure 2-16, substantial cost increases occur during both primary and secondary processing, with costs nearly doubling at each subsequent step, influenced by the number of steps and alloying elements (Roskill Information Services Limited, 2001). A major drawback of cast titanium and its alloys is the large, significantly inhomogeneous grain size in the millimetre range and the preservation of a solidification microstructure and texture (Lütjering, 1998, 1999).

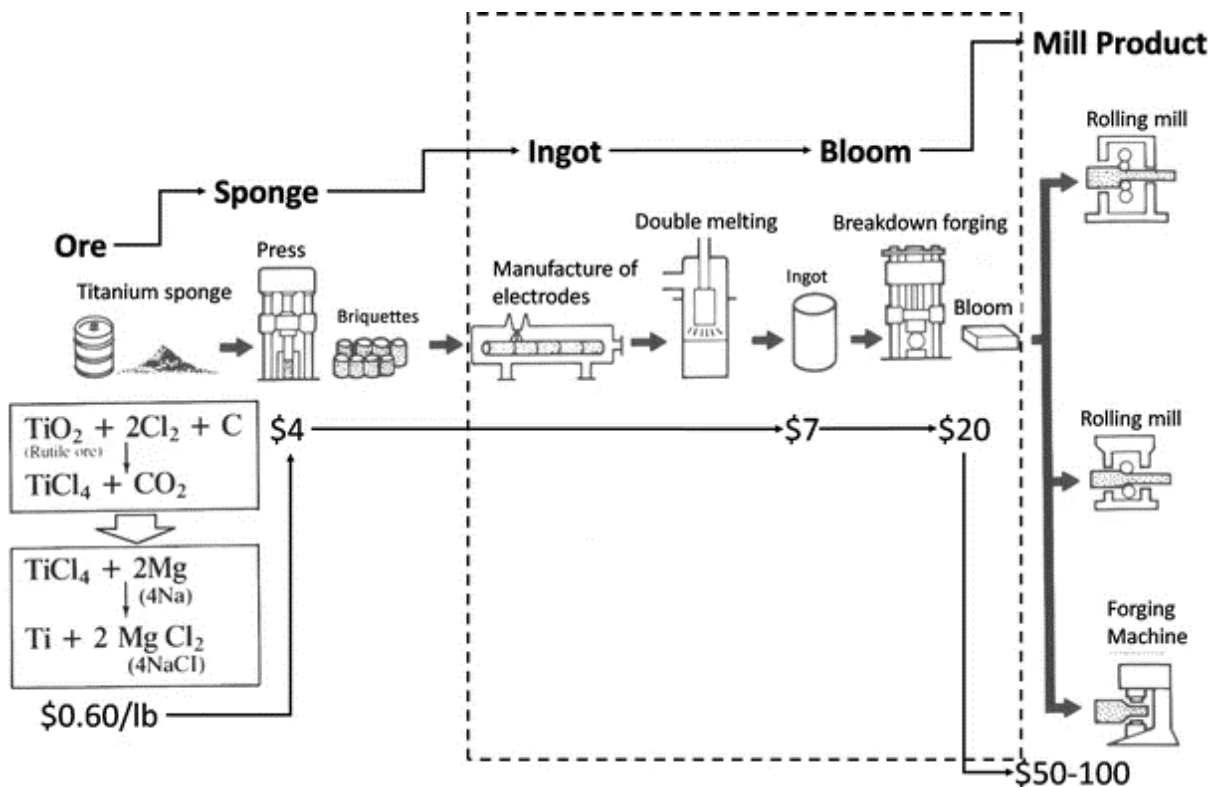


Figure 2-16 A comprehensive overview of the standard titanium processing routine, including a thorough cost assessment for each stage (Roskill Information Services Limited, 2001).

The primary wrought process, known as "ingot breakdown," typically entails significant hot working in the β phase field, leading to dynamic recrystallization. This results in uniform, refined equiaxed grains and a weak texture (Lütjering, 1998, 1999). However, this step is costly, and its elimination could significantly reduce production expenses (Imam et al., 2010). While adding inoculants to various molten metal alloys, such as trace titanium-boron master alloy to aluminium (McCartney, 1989), is a common commercial practice for achieving grain refinement, no such method is employed for titanium alloys. To date, several efforts have been made to refine grains in titanium alloys in the as-cast condition, along with various post-solidification strategies. These latter approaches include thermo-mechanical deformation processing through heat treatment across different phase stability regimes (Kaibyshev, 2001) and severe plastic deformation techniques (Stolyarov et al., 2003). These methods have been successfully applied to various titanium alloys (Perez-Bravo et al., 2005; J. Yang et al., 2003). Additionally, heat treatment in the presence of hydrogen can also lead to grain refinement in titanium alloys (Yoshimura, 1997).

A distinct method involves incorporating specific alloying elements into the initial material to act as grain refiners. Effective grain refinement has been observed in various titanium-aluminide based intermetallics through systematic alloying with elements such as Magnesium (F. S. Sun & Froes, 2003), Antimony (B. Y. Huang et al., 1999), Neodymium (F. S. Sun et al., 2002), and Boron (Cheng, 2000; D. Hu, 2001; Imayev et al., 2007). The addition of boron, in particular, has shown significant impact on titanium-aluminium-niobium (Hecht et al., 2008; Z. X. Li & Cao, 2005).

2.3.1 Metallurgy of Ti-B Alloys

Based on its electronic structure, boron is classified as an α stabilizer with limited α stability (Mcquillan & Mcquillan, 1956). The ratio of atomic radii between boron and titanium is 0.66, hindering the formation of substitutional or interstitial solid solutions with either α or β phases highly unlikely (Hyman et al., 1989). Research by Palty et al. (Palty et al., 1954) examined the solubility of boron in titanium at varying temperatures. They found that boron's solubility in the β phase is nearly 0.05% at 1400°C and slightly above 0.1% at 1660°C, while in the α phase, it remains below 0.05% near the peritectoid reaction. The negligible solid solubility of boron in titanium prevents the embrittlement typically caused by other interstitial elements such as hydrogen, carbon, or oxygen.

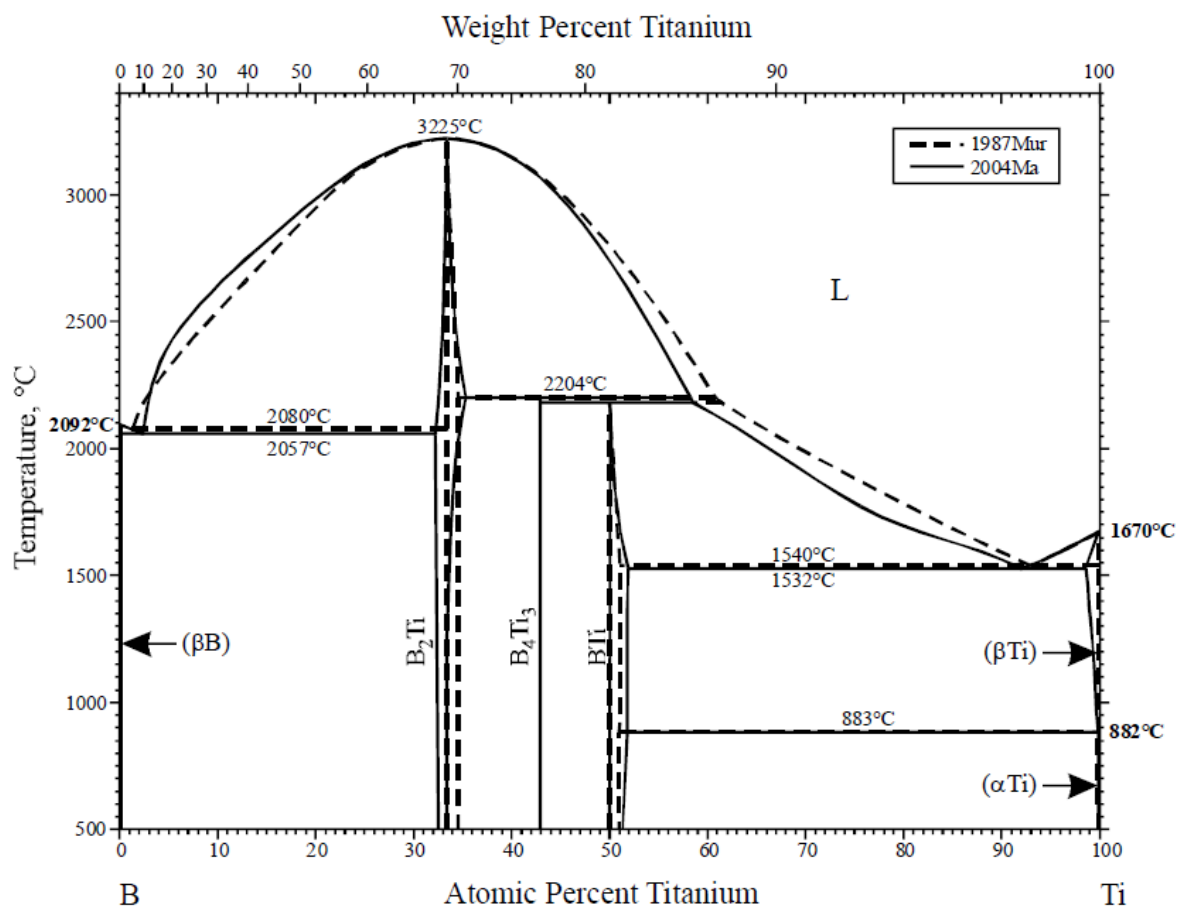


Figure 2-17 Binary equilibrium Ti-B phase diagram (Hiroaki Okamoto, 2016).

Although Ti-Al-V-B alloy phase diagram has not been established, the binary Ti-B phase diagram (Figure 2-17) offers a useful reference for understanding the solidification sequence in such alloy systems (Murray et al., 1986). The phase diagram illustrates three intermetallic compounds: TiB, TiB₂, and Ti₃B₄, alongside terminal phases. The boron weight percentages for these compounds are: TiB at 18 to 18.5%, TiB₂ at 22.4%, and Ti₃B₄ between 30.1 and 31.1% (Panda & Ravi Chandran, 2003). Ma et al. (Ma et al., 2004) have summarized the invariant phase reactions in the TiB system, as detailed in Table 2-2. This table also includes the type of reaction and the temperature at which each reaction occurs. The key reactions in the titanium-boron system are:

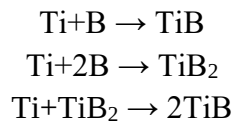


Table 2-2 Various reactions in the Ti-B system (Hyman et al., 1989; Ma et al., 2004).

Reactions	T(°C)	Type	at.%B
Liquid $\leftrightarrow$ TiB ₂	3225±25	Congruent	66.7
Liquid+TiB ₂ $\leftrightarrow$ Ti ₃ B ₄	2200±25	Peritectic	65.5
Liquid+Ti ₃ B ₄ $\leftrightarrow$ TiB	2180	Peritectic	58.1
Liquid $\leftrightarrow$ TiB ₂ +β _{Ti}	2080±20	Eutectic	100
Liquid $\leftrightarrow$ β _{Ti} +TiB	1540±10	Eutectic	<1
β _{Ti} +TiB $\leftrightarrow$ α _{Ti}	884.2	Peritectoid	49
Liquid $\leftrightarrow$ β _{Ti}	1670	Melting point	0
β _{Ti} $\leftrightarrow$ α _{Ti}	882	Allotropic	0
Liquid $\leftrightarrow$ β _B	2092	Melting point	100

Figure 2-18 presents the free energy of formation as a function of temperature for TiB and TiB₂, highlighting that the formation of TiB₂ has the most negative ΔG among these reactions. However, TiB₂ is unstable in molten titanium due to thermodynamic reasons, specifically because the reaction Ti+TiB₂ → 2TiB has a slightly negative ΔG. This thermodynamic favourability causes TiB₂ to further convert to the more stable TiB phase. Leveraging this instability, TiB₂ can be utilized as a boron source to produce TiB (Panda & Ravi Chandran, 2003).

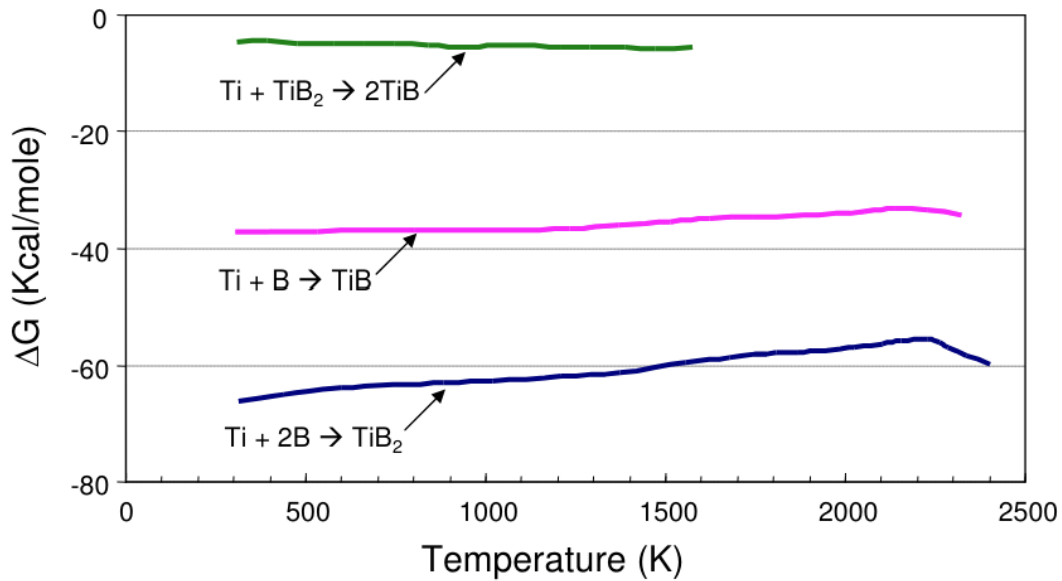


Figure 2-18 Gibbs free energy of Ti-B compounds as a function of processing temperatures (Panda & Ravi Chandran, 2003).

2.3.2 Crystallography of TiB

The composition ranges, lattice parameters and space groups for Ti_xB_y compounds are given in Table 2-3 (Ma et al., 2004; Murray et al., 1986; Panda & Ravi Chandran, 2003). In the Ti-B system, the primary intermetallic compounds are TiB and TiB_2 . These compounds are characterized by their extreme hardness, excellent electrical conductivity, strong resistance to thermal shock, high melting points, chemical inertness, and exceptional durability.

Table 2-3 Composition ranges, lattice parameters and space groups for various compounds in Ti-B system (Ma et al., 2004).

Phase	Composition Range (wt.%B)	Space Group	Lattice Parameter (nm)		
			<i>a</i>	<i>b</i>	<i>c</i>
TiB	18-18.5	Pnma	0.612	0.306	0.456
TiB_2	22.4	P6/mmm	0.302	0.323	0.454
Ti_3B_4	30.1-31.1	Immm	0.325	1.373	0.322

The crystal structures of TiB and TiB_2 are illustrated in Figure 2-19. Both structures are derived from a fundamental unit: a trigonal prismatic arrangement of six titanium atoms with a central boron atom (De Graef et al., 1992). TiB has a B27 structure, characterized by closely packed trigonal prisms aligned in one direction, forming columns on a rectangular base and connecting only at their edges (Feng, Zhou, Jia, & Meng, 2006). Figure 2-19 depicts the arrangement of Ti and boron atoms in the B27 structure. The trigonal prisms are distorted because the rectangular prism faces parallel to [010] are stretched in that direction, causing the boron atoms in each prism to shift towards the elongated face (Hyman et al., 1989). TiB_2 features a C32 structure, also shown in Figure 2-19. In this structure, the trigonal prisms are close-packed, sharing faces with adjacent prisms. The boron atoms form planes like graphite, as illustrated in Figure 3.7 (Hyman et al., 1989).

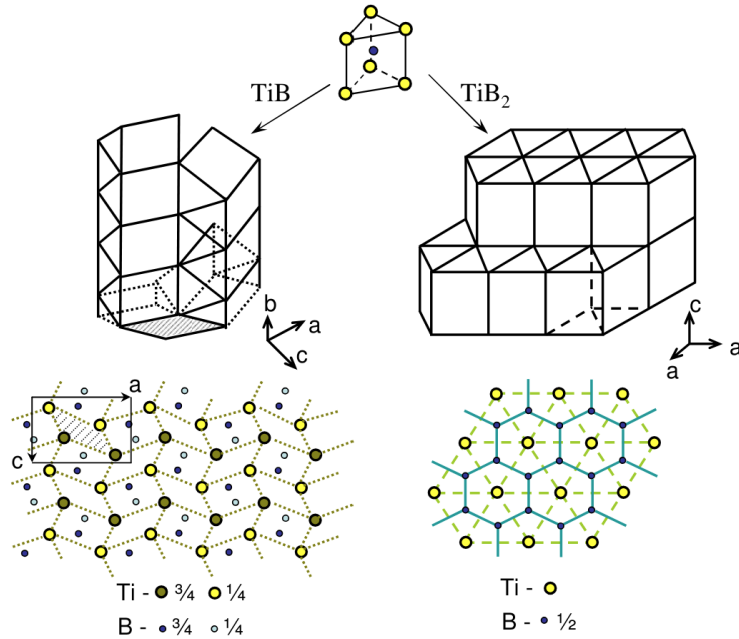


Figure 2-19 Crystal structures of TiB and TiB₂ (Hyman et al., 1989).

2.3.3 Microstructures of Boron Modified Titanium Alloys

Microstructural examinations of cast Ti6Al4V alloy with varying levels of boron addition in the hypoeutectic range demonstrated significant refinement compared to the alloy without boron (Sen et al., 2007; Tamirisakandala, Bhat, Tiley, et al., 2010). Both Ti6Al4V alloys, with and without boron, exhibited a lamellar microstructure featuring alternating layers of α and β phases within a colony. The microstructural refinement was observed in both the prior- β grain size and the α colony size (Figure 2-20). In boron-containing alloys, the Widmanstätten α colony structure forms within the prior- β grain, while the TiB phase appears as whiskers with an aspect ratio of approximately 8–9, primarily located at the prior- β grain boundaries in a necklace-like arrangement. The microstructure of the alloy without boron features a thick α_{GB} layer ($\sim 10 \mu\text{m}$), whereas alloys with boron show a significant reduction in this microconstituent size. Thus, the addition of boron may help eliminate or disrupt α_{GB} phase network. Similar microstructures have also been reported for various other ($\alpha+\beta$) alloys with hypoeutectic boron addition (Chandravanshi et al., 2011; K. Prasad et al., 2011).

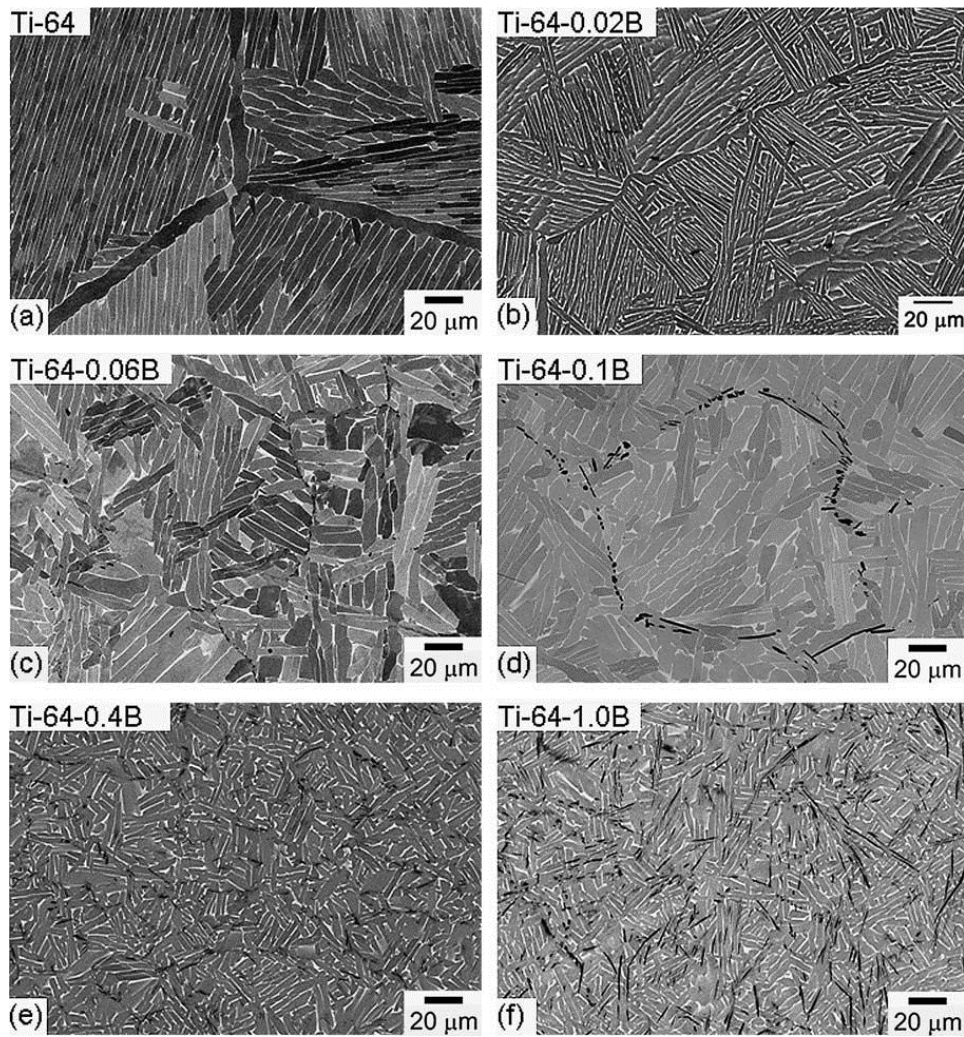


Figure 2-20 Backscattered electron images of cast Ti6Al4V containing boron levels indicated on the micrographs. The grey background is the α , bright phase is the β , and dark black phase is the TiB (Tamirisakandala et al., 2005).

The development of microstructural features across various length scales in α , $\alpha+\beta$, and β -titanium alloys is primarily influenced by factors such as the alloy type, the thermo-mechanical processing route used, the degree of reduction, the cooling rate, and the annealing temperature (Lütjering & Williams, 2007). Various studies have summarized the effects of boron additions on different microstructural parameters in α , $\alpha+\beta$, and β -titanium alloys. Parameters such as α grain size (d_α), α colony size (c), prior- β grain size (d_β), Volume fraction of TiB needles (V_{TiB}) and aspect ratio of TiB needles (S_{TiB}) have been analysed. The findings indicate that minor additions of boron not only refine the as-cast β grain size but also decrease other microstructural length scales, leading to an overall improvement in the alloy microstructure. Figure 2-21 illustrates the variations of d_β and c in as-cast Ti6Al4V alloy as a function of boron content (Sen et al., 2010). Both d_β and c show a similar trend with boron content because α colonies nucleate and grow near these prior- β grain boundaries (Appolaire et al., 2005). Conversely, the variation in d_α with boron content in titanium alloys seems to be more influenced by the cooling rate during solidification (M. Bermingham, McDonald, Nogita, et al., 2008). Interestingly, the aspect ratio of α laths (S_α) appears to be affected by boron addition. In the boron-free alloy, α

laths are long and thin, whereas in boron-containing alloys, they are short and thick, as shown in Figure 2-20 (Tamirisakandala, et al., 2005). A close examination of the microstructural parameters of wrought alloys studied reveals d_β or d_α obtained after thermo-mechanical processing and heat treatment are not significantly affected by boron addition, as they remain similar to those in the boron-free alloy. This is because substantial grain refinement has already occurred during the casting stage of the boron-containing alloy, so subsequent processing steps result in only marginal refinement.

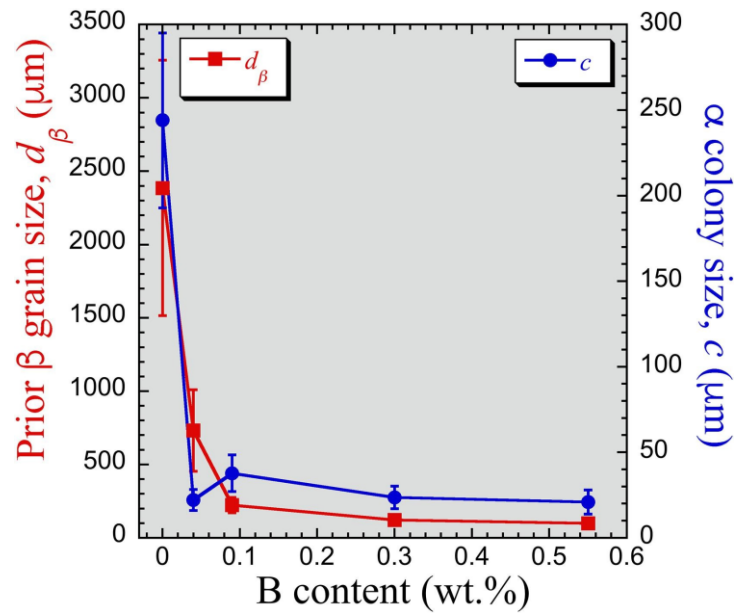


Figure 2-21 The relationship between the initial β grain size and the α colony size with varying boron content in the as-cast Ti6Al4V alloy (Sen et al., 2010).

2.3.4 Effect of TiB Needles on the Morphology of α -phase

It has been extensively documented TiB needles provide additional heterogeneous nucleation sites for the α phase, modifying its morphology from the traditional lath-like structure to a more equiaxed form during slow cooling from the $\beta \rightarrow \alpha$ transformation in various titanium alloys (Hill et al., 2005; L. J. Huang et al., 2009; Nandwana et al., 2012; Sasaki et al., 2011; Y. Yang et al., 2013). The low lattice mismatch between TiB and α phases (less than 3.6%) facilitates this heterogeneous nucleation of α -phase (Y. Yang et al., 2013). Hill et al. (Hill et al., 2005) were the first to observe a morphological shift to coarse equiaxed α instead of lamellar in the furnace-cooled ($\sim 5^\circ\text{C}/\text{min}$) Ti6Al4V alloy with 4% V_{TiB} . Nandwana et al. (Nandwana et al., 2012) conducted an in-depth analysis of the crystallographic orientation relationships between the TiB, α , and β phases influencing the morphology of α nucleating at TiB needles in Ti5553-0.5B alloy using EBSD OM technique. Figure 2-22(a) and (b) present pseudo-coloured OM maps of two distinct regions, showcasing α precipitates in equiaxed and lath-like morphologies. In these figures, α_1 , α_2 , and α_3 are variants of α precipitates associated with TiB needles. In Figure 2-22(a), α precipitates with equiaxed morphology are visible, where TiB needles exhibit distinct ORs with all three α precipitates. These ORs are:

$$\begin{aligned}
&(0001)_\alpha \parallel (001)_{\text{TiB}} \text{ and } \langle 11\bar{2}0 \rangle_\alpha \parallel [010]_{\text{TiB}}; \\
&(0001)_\alpha \parallel (101)_{\text{TiB}} \text{ and } \langle 11\bar{2}0 \rangle_\alpha \parallel [010]_{\text{TiB}}; \\
&\langle 01\bar{1}1 \rangle_\alpha \parallel (001)_{\text{TiB}} \text{ and } \langle 11\bar{2}0 \rangle_\alpha \parallel [010]_{\text{TiB}}
\end{aligned}$$

for α_1 , α_2 , and α_3 , respectively. However, ORs between TiB/ β and BORs between the three α precipitates and β are not observed (Burgers, 1934). Similar analysis on α precipitates (α_1 and α_2) with lath-like morphology in Figure 2-22(b) indicates the presence of ORs between TiB/ α and TiB/ β , specifically $(011)_\beta \parallel (001)_{\text{TiB}}$ and $\langle 111 \rangle_\beta \parallel [010]_{\text{TiB}}$ (Nandwana et al., 2012). Consequently, BORs between β and α phases are maintained. This contrasts with the equiaxed morphology of α seen in Figure 2-22(a), where β does not exhibit OR with either the TiB needle or the α precipitates. In summary, the presence or absence of ORs between TiB/ β significantly influences the α morphology. Equiaxed α results when TiB needles do not maintain specific ORs with adjacent β , whereas a lath-like morphology forms if BORs between α precipitates and β are maintained (Nandwana et al., 2012). This is particularly noteworthy because equiaxed α forms near TiB needles in Ti5553-0.5B without the need for mechanical working or recrystallization in the α + β field.

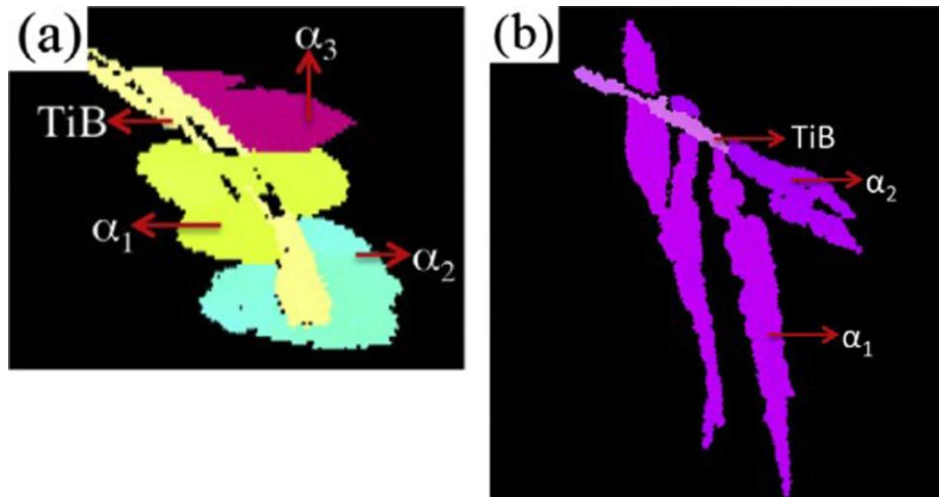


Figure 2-22 Pseudo-coloured OM maps of the Ti5553-0.5B alloy depict (a) an equiaxed and (b) a lath-like structure of α precipitates surrounding TiB needles (Nandwana et al., 2012).

2.3.5 Effect of Boron Additions on the β_{transus} Temperature

The β_{transus} temperature (T_β) at which hcp- α phase fully converts to bcc- β phase is a crucial factor in the thermo-mechanical processing of titanium alloys (Tamirisakandala, et al., 2005; Weiss & Semiatin, 1998, 1999). The microstructure developing during this processing, along with the optimal α/β phase ratio, is highly sensitive to the processing temperature in relation to the T_β (Semiatin et al., 1997), which itself is influenced by the concentrations of α and β stabilizers in the alloy (Welsch et al., 1993). α stabilizers such as aluminium, oxygen, and nitrogen increase β_{transus} temperature compared to pure titanium, while β stabilizers like vanadium, molybdenum (Leyens & Peters, 2006) lower T_β (Leyens & Peters, 2006). To estimate T_β based on the alloy composition, the following empirical relationship is frequently used (Z. Guo et al., 2005):

$$T_{\beta} (^{\circ}\text{C}) = 882 + 21.1[\text{Al}] - 9.5[\text{Mo}] + 4.2[\text{Sn}] - 6.9[\text{Zr}] - 11.8[\text{V}] - 12.1[\text{Cr}] - 15.4[\text{Fe}] + 23.3[\text{Si}] + 123.0[\text{O}] \quad 2.2$$

It is well recognized the T_{β} of titanium alloys is significantly affected by the interstitial oxygen content. This influence is clearly demonstrated by the high oxygen coefficient in Equation 2.2. As an illustration, raising the oxygen content from 1100ppm (ELI grade) to 1800ppm (commercial grade) can elevate T_{β} by approximately 50°C (Y. V. R. K. Prasad et al., 2001).

The influence of boron on the T_{β} is limited due to its minimal solid solubility (Mcquillan & Mcquillan, 1956). However, an exception was noted by Seshacharayalu et al. (2001) in the case of rapidly solidified and powder metallurgy processed hypereutectic Ti6Al4V alloy. For the boron-modified alloy, an increase of approximately 60°C in the T_{β} was observed, which was attributed to the supersaturation of boron in the microstructure resulting from the extremely high cooling rate used. In contrast, for the cast Ti6Al4V-0.1B alloy, boron addition can cause the T_{β} to exceed that predicted by composition, due to microstructural factors significantly delaying the $\alpha \rightarrow \beta$ transformation locally (Roy, Tungala, et al., 2011). Ivasishin et al. (Ivasishin et al., 2008) suggested the slight increase in T_{β} with boron addition in as-cast Ti6Al4V is due to the redistribution of aluminium and vanadium concentrations. EPMA analyses of the α , β , and TiB phases show that boron addition leads to the depletion of titanium from the matrix, accompanied by an increase in aluminium in the α phase and vanadium in the β phase (Ivasishin et al., 2008; G. Singh et al., 2014). This effect could be counterbalanced if aluminium and vanadium were soluble in the TiB phase. However, Ivasishin et al. (Ivasishin et al., 2008) found an average vanadium content of only 3.3 wt% in the TiB phase, with aluminium undetectable. Therefore, the slight shift in T_{β} with boron addition is likely due to the increased aluminium concentration in the α phase. This conclusion is supported by the empirical relationship indicating that 1 wt% aluminium raises T_{β} by 16.7°C, while 1 wt.%V lowers T_{β} by 9.1°C (Z. Guo et al., 2005).

2.3.6 Grain Refinement Effect

The large prior- β grain size in cast titanium alloys presents difficulties for secondary processing of the ingot. Moreover, titanium alloys in their cast state display uneven solidification textures: a $\langle 100 \rangle$ fiber texture in the columnar β grain regions and a weak or random texture within the interior of ingot (Glavicic et al., 2003). As a result, titanium alloys undergo multiple thermo-mechanical processing steps to disrupt the as-cast structure, randomize the texture, and develop fine microstructures in the alloys.

Over the past twenty years, numerous studies have demonstrated that minor additions of boron to various titanium alloys, including near- α , $\alpha + \beta$, and β alloys, significantly refine their microstructure in the as-cast state (Chandravanshi et al., 2010, 2011; Kim et al., 2014; Pederson et al., 2012; K. Prasad et al., 2011; Sarkar et al., 2013; Tamirisakandala, et al., 2005. Recently, Zhu et al. (J. Zhu et al., 2003) reported trace amounts of boron lead to grain refinement in titanium-based alloys. They observed substantial microstructural refinement in cast titanium and Ti-0.5Si alloys with hypoeutectic (~0.086 to 0.14 wt.%) boron additions. Similar results

were reported for ($\alpha+\beta$) titanium alloys such as Ti6Al4V (M. Bermingham, ..., et al., n.d.), Ti6Al2Sn4Zr2Mo (Tamirisakandala, et al., 2005), Ti6Al5Zr0.5Mo0.25Si (Chandravanshi et al., 2010), Ti1100(Chandravanshi et al., 2011), and Timetal 834 (K. Prasad et al., 2011), as well as β alloys like Ti15Mo2.6Nb3Al0.2Si(Sasaki et al., 2011; Tamirisakandala et al., 2005) and Ti5Al5Mo5V3Cr (Tamirisakandala et al., 2005). Even boron additions as low as 0.04 wt.% can produce significant β grain refinement in cast conditions, which would otherwise require multiple primary ingot breaking steps (Tamirisakandala, et al., 2005). For instance, adding approximately 0.1 wt.%B reduces the cast β grain size from 1700 μm to 200 μm in Ti6Al4V, from 550 μm to 50 μm in Ti-6242, from 500 μm to 50 μm in CP titanium, and from 300 μm to 50 μm in Ti-5553 alloys. Figure 2-23(a) illustrates the variation in prior β size for these commercial titanium alloys with boron addition, while Figure 2-23(b) shows polarized light micrographs depicting the impact of boron on α -colony size for Ti6Al4V and Ti-6242 alloys. A detailed analysis of Figure 2-23(a) shows a distinct change in the grain size versus boron content plot within the range of approximately 0.04–0.1 wt.%B.

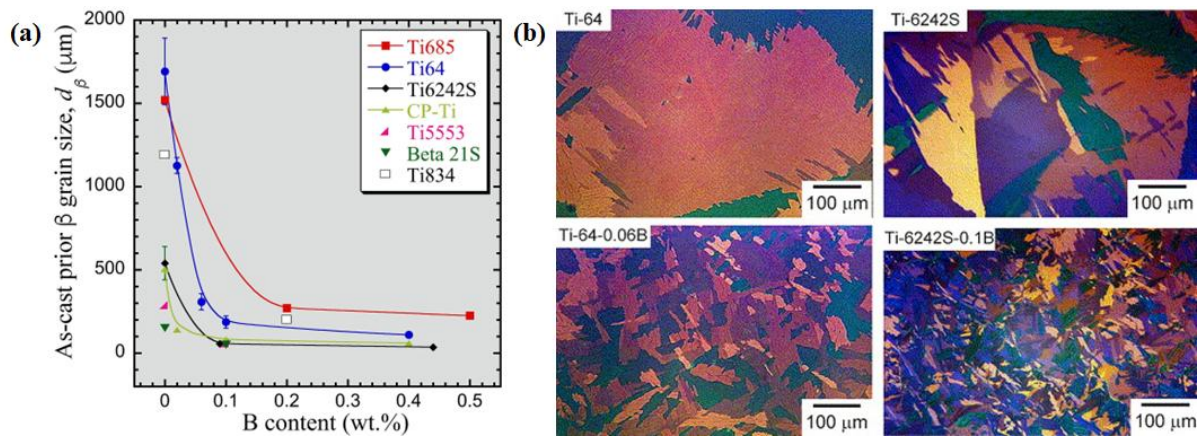


Figure 2-23 (a) Variation of cast β grain size with boron concentration in various commercial titanium alloy and (b) polarized light micrographs of cast Ti6Al4V and Ti-6242 alloys(Tamirisakandala, et al., 2005).

The mechanism for grain refinement of cast titanium alloys via boron addition is hypothesized based on similar mechanisms originally proposed for titanium-aluminium intermetallic alloys (Cheng, 2000). This hypothesis posits the grain refinement process is essentially a dynamic equilibrium between solute rejection at the solidification front, the formation of borides, and nucleation ahead of the front. Tamirisakandala et al. (Tamirisakandala & Miracle, 2010) proposed a grain refinement mechanism for titanium alloys. The diagram in Figure 2-24(a) illustrates the grain refinement process for Ti6Al4V alloy. Above the T_{liquidus} , boron is fully dissolved in the liquid. During cooling, primary β nuclei begin to nucleate and grow within the temperature range between the T_{eutectic} and T_{liquidus} . In this state, boron is strongly expelled from the nuclei due to its low solubility in β titanium, leading to solute partitioning in the liquid ahead of the solidification front. This results in an increased solute concentration around the growing β nuclei, causing constitutional supercooling, which destabilizes the liquid/solid interface and promotes further β grain nucleation. As solidification advances, the constitutional supercooling enhances the driving force for the nucleation of new β nuclei in front of the liquid/solid interface, simultaneously decelerating the growth kinetics of the existing

liquid/solid interface. The resulting β grain size is determined by the balance between nucleation and growth rates. As the temperature decreases further below the T_{eutectic} , a eutectic mixture of (TiB + eutectic β) forms between the primary β grains. Below the β_{transus} temperature, the β phase undergoes an allotropic transformation into the α phase. During this transformation, different α variants nucleate simultaneously at the prior- β grain boundaries and grow inside the β grains until they intersect (Chesnutt et al., 1976). This leads to a nearly one-to-one correspondence between the sizes of the original β grains and the resulting α colonies, assuming all α variants are equally represented in the microstructure (Stanford & Bate, 2004). Consequently, the refinement of the prior β grain size translates into a refined α colony size. It is notable that, since the TiB phase forms after the primary β phase in hypoeutectic compositions, TiB particles do not serve as nucleation sites for β grain formation, and grain refinement through inoculation does not occur. The solidification sequence for such a hypoeutectic composition is schematically depicted in Figure 2-24(b).

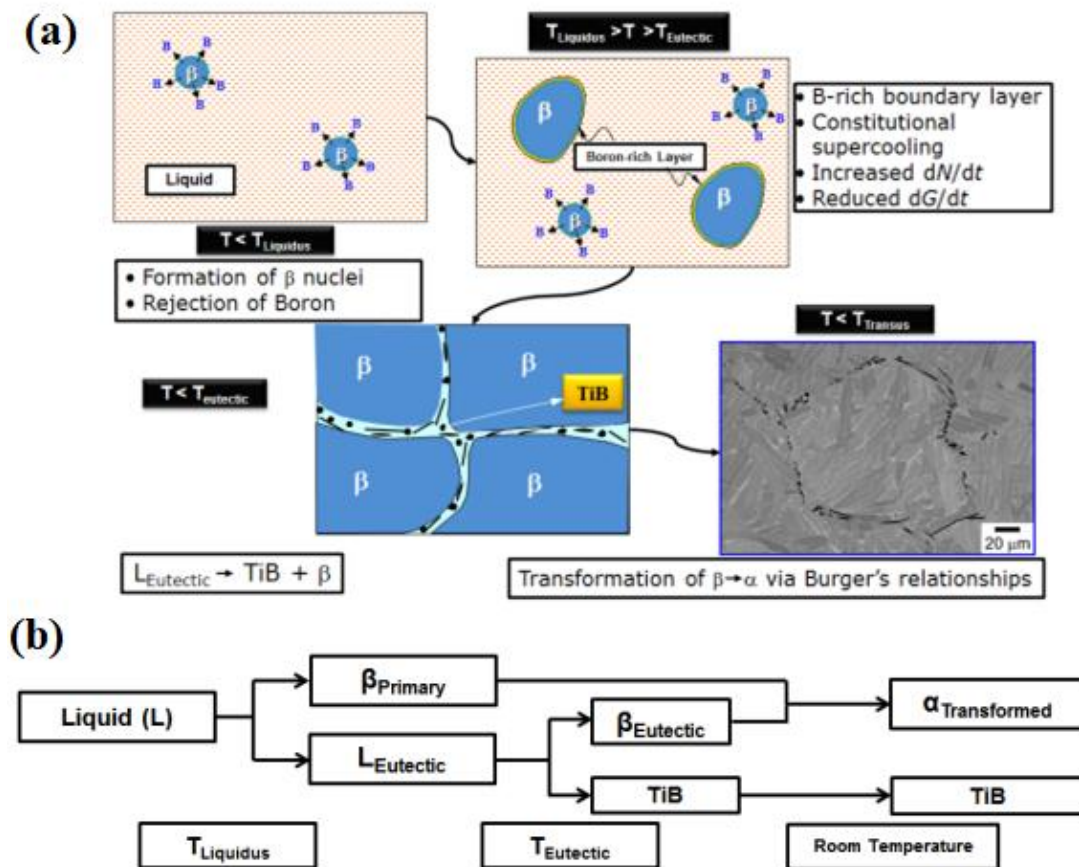


Figure 2-24 Schematic showing (a) grain refinement mechanism; (b) solidification sequence in a boron modified titanium alloy (Tamirisakandala & Miracle, 2010).

The phenomenon of constitutional supercooling is central to understanding the grain refinement effect of boron in titanium alloys. The solidification process of alloys is influenced by the diffusion of solute into the liquid, similar to how latent heat is removed in pure metals, as well as by the temperature gradient within the solidifying liquid (Porter et al., 2009). Before the solidification front, there is a variation in the solute concentration of the liquid (Figure

2-25(a)), resulting in the equilibrium solidification temperature (T_E) varying with distance from the solidification front (Figure 2-25(b)). The liquid temperature (T_L) also changes with distance, creating a temperature gradient within the liquid. The solidification behaviour is determined by comparing the liquid temperature with the equilibrium solidification temperature.

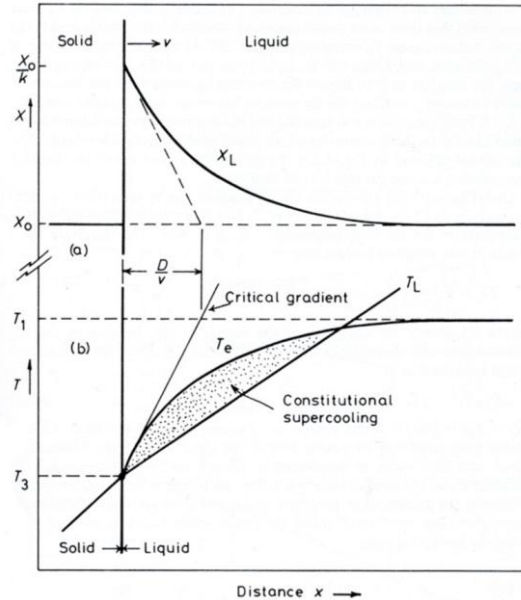


Figure 2-25 Constitutional supercooling occurs in front of a planar solidification interface, illustrated by (a) the composition gradient and (b) the thermal gradient. Here, T_E represents the equilibrium solidification temperature, and T_L denotes the liquid temperature (Porter et al., 2009).

If the liquid temperature is below the equilibrium temperature, the liquid is in a supercooled state due to compositional or constitutional effects, a phenomenon known as constitutional supercooling. Stable non-planar growth can only form under these conditions. As shown in Figure 2-25, the tip of any forming protuberance will have a higher temperature than the planar front. However, solidification can still occur if the tip temperature remains below T_E , allowing the tip to grow in a cellular or dendritic manner. The extent to which a solute contributes to constitutional supercooling can be forecasted using the growth restriction factor Q (M. Bermingham, McDonald, Nogita, et al., 2008.; Tamirisakandala, Bhat, Tiley, et al., 2005):

$$Q = m_l C_0 (1 - k) \quad 2.3$$

where m_l represents the slope of the liquidus, C_0 is the solute concentration, and k is the partition coefficient. Solutes characterized by a high growth restriction factor tend to partition significantly ahead of the solid/liquid interface, leading to a pronounced degree of constitutional supercooling (M. Bermingham, McDonald, Nogita, et al., 2008). In titanium alloys, adding boron affects the solute content and equilibrium solidification temperature, optimizing conditions for constitutional supercooling. This promotes non-planar growth and results in finer grain structures. However, there is a critical boron content level necessary for optimal grain refinement (Tamirisakandala & Miracle, 2010). Increasing the boron content beyond this critical level (~ 0.1 wt.%) leads to only a slight decrease in grain size

(Tamirisakandala et al., 2005). Thus, the controlled addition of boron facilitates constitutional supercooling, which is crucial for achieving effective grain refinement in titanium alloys.

2.3.7 Advantages of Boron Additions in Titanium Alloys

Depending on the alloying element content, various types of precipitates can be stabilized within the titanium-boron system. The volume fraction of these precipitates determines if the system meets the criteria for an alloy or a composite. Hyper-eutectic compositions exhibit microstructures and properties akin to those found in discontinuously reinforced MMCs, categorizing them as composites. In contrast, hypo-eutectic compositions, with a maximum of 1.55 wt.%B for the Ti6Al4V alloy and TiB volume fractions under approximately 8%, are considered boron-modified alloys (Ivasishin et al., 2008). In addition to microstructural refinements, TiB phase stands out by offering several unique advantages compared to other compounds within the titanium-boron system. The most important ones are summarized as follows:

1. Boron does not dissolve in either the α or β phases (Palty et al., 1954), meaning all the added boron forms TiB needles. This avoids the issue of lattice embrittlement, occurring with interstitial elements like H, O, N, and C when they exceed their allowable limits.
2. TiB needles develop as short whiskers, providing efficient strengthening due to their high hardness.
3. The coefficient of thermal expansion of TiB closely matches that of titanium reducing thermal residual stresses during cooling from the $\beta/\alpha+\beta$ phase.
4. TiB needles at the grain boundaries hinder their mobility at elevated temperatures through the Zener drag mechanism (Bhat et al., 2004; Cherukuri et al., 2009).
5. TiB reinforcement maintains both mechanical and chemical stability. The interface between Ti and TiB needles is clean (Feng, Zhou, Jia, Meng, et al., 2006a; D. X. Li et al., 1993a), without the formation of intermediate phases seen with reinforcements like SiC, Al₂O₃, and Ti₃N₄ (Gorsse & Le Petitcorps, 1998; Tjong & Mai, 2008; Tressler et al., 1973; Y. Q. Yang et al., 1998).
6. The specific strength (σ_y/ρ) and specific stiffness (E/ρ) of titanium alloys are enhanced without increasing weight, as the densities of TiB and titanium are nearly identical (Ravi Chandran et al., 2004).

Titanium alloys are prone to rapid grain coarsening at high temperatures, especially in the β phase (Gil & Planell, 2000). Cherukuri et al. (Cherukuri et al., 2009) studied the effect of TiB needles on the grain growth kinetics of the Beta 21S-0.1B alloy. They annealed the alloy with 0 and 0.1 wt.%B for durations ranging from 30 minutes to 10 hours at temperatures exceeding their T_β . Their results showed that in the boron-free alloy, annealing significantly increased grain size. Conversely, the prior- β size of the Beta 21S-0.1B alloy remained unchanged across all annealing temperature-time combinations. A similar observation was noted in Ti6Al4V-1B alloy processed by powder metallurgy, where the average prior- β size remained constant after thermal exposure at 1200 °C for 1 hour (McEldowney et al., 2010; Tamirisakandala & Miracle, 2012). Cherukuri et al. attributed this to the Zener pinning effect of TiB needles located at the

β grain boundaries and modelled it with a modified Zener drag model considering factors such as volume fraction and aspect ratio of TiB needles, and the orientation of TiB needles relative to the grain boundary (Cherukuri et al., 2009). The necklace-like network of TiB needles at the β grain boundaries might also provide additional resistance to grain growth.

Previous studies on various titanium-based intermetallic alloys have demonstrated boron segregates to grain boundaries, enhancing their cohesive strength and thereby reducing intergranular failure (Baker et al., 1989; L. Huang et al., 2012; Mills et al., 1991; F. Tang et al., 2001). For instance, Tang et al. (F. Tang et al., 2001) observed adding 0.2 at.%B to Ti-22Al-20Nb-2W (at.%), O+B2-based Ti aluminide alloy, increased its ductility from 0.8% to 3.4%. At this low boron concentration, boron atoms were found to segregate at the B2 grain boundaries. Luan et al. (Luan et al., 2015) also studied the grain boundary chemistry of tensile fracture surfaces in as-cast Ti6Al4V alloy with 0, 0.02, and 0.05 wt.%B contents using Auger Electron Spectroscopy. The presence of boron peaks in the Auger spectra at the grain boundaries of the 0.02 and 0.05B alloys confirms boron indeed segregates to the grain boundaries in cast Ti6Al4V alloys, enhancing their cohesive strength (Luan et al., 2015). Consequently, the fracture mode shifted from intergranular in the boron-free alloy to predominantly transgranular in the boron-modified alloys. The boron peaks in the transgranular regions were primarily attributed to TiB needles. Quantitative analysis further revealed the relative concentration of boron in the transgranular region (mainly from TiB) was significantly higher compared to the grain boundary region (Luan et al., 2015). Thus, the improved ductility in as-cast titanium alloys with trace boron additions cannot be solely attributed to grain size refinements. The enhancement in the cohesive strength of β grain boundaries due to boron segregation also plays a crucial role (Luan et al., 2015).

2.4 Metal Additive Manufacturing Methods

Additive manufacturing technologies can be classified based on the energy sources used and the feedstock forms involved. Common feedstock forms include powders, wires, and sheets, while energy sources typically consist of laser beams (D. D. Gu et al., 2012), electron beams (Raghavan et al., 2016), or electric arcs (Cunningham et al., 2018). Melting-based AM techniques, such as powder bed fusion and directed energy deposition, are widely adopted for fabricating metallic components from alloys based on titanium, steel, nickel, aluminium, and high entropy alloys (Lewandowski & Seifi, 2016). Alternatively, binder jetting employs a liquid binding agent to join powder particles, followed by a subsequent sintering step to achieve densification, whereas sheet-based AM techniques build components through lamination of metal sheets. Within the scope of this thesis, particular emphasis is placed on PBF-LB/M, focusing on the production of titanium-based alloys owing to their extensive use in aerospace and biomedical applications (Z. Z. Fang et al., 2018). A brief overview of metal additive manufacturing methods relevant to this research is presented in the following section.

2.4.1 Powder Bed Fusion

Powder bed fusion techniques fabricate three-dimensional structures by selectively fusing powder particles using thermal energy applied in a layer-by-layer manner. This fusion can

occur either through complete melting, commonly applied to metallic powders (laser powder bed fusion or electron beam melting) (Yap et al., 2015), or through partial melting or sintering, which is predominantly used for polymeric materials (Beaman & Deckard, 1989). To achieve high dimensional accuracy, the thermal energy must be precisely focused, typically using either a laser or electron beam source. Such precise focusing ensures controlled consolidation, maintaining accurate final dimensions. Laser beams, in particular, are widely utilized, offering excellent precision and control for metal additive manufacturing. Alternatively, electron beam systems can also be employed for metallic materials requiring different processing conditions.

2.4.1.1 Laser Powder Bed Fusion (PBF-LB/M)

PBF-LB/M is an established additive manufacturing method that is comprised of multiple stages, allowing the fabrication of intricate metal components. The main steps involved include preparation and distribution of powder, creation of a computer-controlled CAD/CAM model, application of specific laser scanning strategies, and post-processing treatments. A detailed schematic and workflow of the PBF-LB/M process is illustrated in Figure 2-26. In this process, a thin powder layer is evenly spread across a substrate or base plate, where consistent powder layering and precise control of layer thickness are critical to achieving homogeneous fusion and successful consolidation of the metal particles (Herzog et al., 2016; Yap et al., 2015).

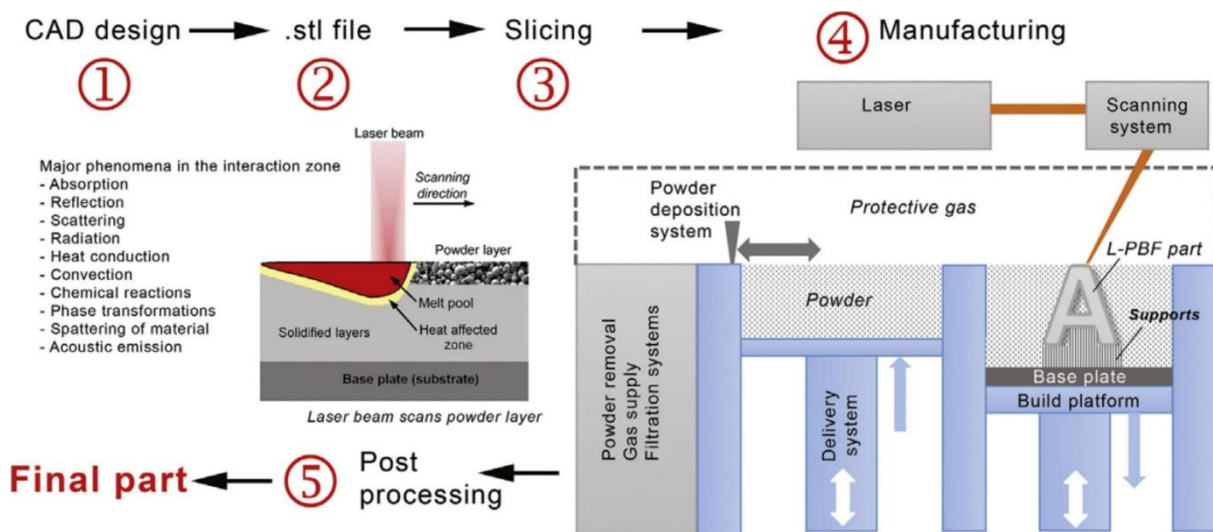


Figure 2-26 Step-by-step process and visual diagram showing how lasers melt and fuse powdered materials layer by layer in PBF-LB/M (Yadroitsev et al., 2021).

Powder delivery and recoating systems are employed to ensure consistent powder deposition after each processed layer. A predetermined quantity of powder is dispensed from a reservoir by elevating the piston upward, after which a recoater evenly distributes the powder across the base plate or previously processed layer. After each layer is melted, the build platform descends, allowing the recoater to again deposit powder for subsequent layer formation. Generally, two kinds of recoater are utilized: (i) soft blade recoater and (ii) hard blade recoater. Soft blade recoater, typically composed of rubber or carbon fibre brushes, gently spread powder particles with minimal force applied. It has been reported that soft blade recoater can fabricate

parts with notably high aspect ratios (up to 300:1) and also reduce the need for support structures (Fox et al., 2022). Due to their high flexibility, soft blade recoater do not damage metal parts or cause interruptions in fabrication if collisions with protruding parts or defects occur. However, such defects tend to be amplified during subsequent powder deposition, leading to a defective final component. In contrast, hard blade recoater, usually made of ceramics or tool steel, do not tolerate deformation of the part being fabricated. Consequently, collisions between hard blades and the printed parts necessitate immediate interruption of the process, thus preventing continued production of defective components (Yadroitsev et al., 2021). Nevertheless, the use of hard blade recoater introduces vibrations upon collision with the part, causing uneven powder layers and potentially reducing dimensional accuracy (Daña et al., 2019).

A base plate, attached to the build platform, provides mechanical support for the powder layers being deposited. Typically, the base plate material matches the chemical composition of the powder or at least demonstrates suitable weldability with the feedstock. If the deposited material is brittle or susceptible to cracking, preheating of the base plate is advisable to mitigate residual stresses (Mukherjee et al., 2017). Moreover, preheating contributes an auxiliary heat input, thus promoting better material densification, particularly when initial laser energy alone is insufficient for achieving full density (R. Mertens et al., 2018). For instance, preheating the base plate from 80°C to 200°C can reduce component distortion by approximately 20%, and increasing the preheat temperature further to around 600°C may completely prevent distortion, as observed in the case-hardening steel 16MnCr5 (Schmitt et al., 2020). Due to their substantial surface-to-volume ratio, powder materials are notably sensitive to oxidation. Therefore, inert shielding gases such as nitrogen or argon are utilized during processing to protect the powder from oxidation. Generally, nitrogen is employed with less reactive metals like nickel or cobalt, whereas highly reactive metals such as aluminium or titanium require an argon or helium atmosphere (Amano et al., 2021). The thermal conductivity associated with the selected shielding gas influences the cooling rate and, consequently, alters the thermal equilibrium within the build chamber (Schmitt et al., 2020). Beyond the choice of shielding gas, additional parameters such as the uniformity of gas flow (Y. Yang et al., 2023), the rate at which gas is supplied (Reijonen et al., 2020), and the direction of gas flow (Masoomi et al., 2018) significantly impact the melt pool shape and the overall quality of the manufactured component.

Due to localized heating during the PBF-LB/M process, substantial thermal gradients are generated, resulting in thermal stresses and non-uniform heat distribution across the build. These gradients often cause thermal-induced defects or inconsistencies in the fabricated components, such as residual stresses or distortions. To mitigate these adverse effects, careful selection of scanning strategies is critical for achieving balanced thermal management and uniform temperature distribution (Leary, 2018). Such scanning strategies encompass various process parameters, including scan vector length (Gokcekaya et al., 2020), hatch distance (W. Shao et al., 2022), scanning direction rotations (Leicht et al., 2020; Thijs et al., 2013), and scanning sequences (Foteinopoulos et al., 2020; Jia et al., 2021). During fabrication, the laser selectively melts powder layers and inherently involves complex physical interactions,

including re-solidification of molten pools. This process combines phenomena from multiple scientific disciplines, such as heat transfer mechanisms influencing thermal conduction (Manvatkar et al., 2014) and fluid flow, thermally induced phase transformations (Kumara et al., 2020), melt-pool dynamics involving spattering phenomena (Manvatkar et al., 2015), and chemical reactions within the melt pool (A. I. Mertens et al., 2016). Additionally, understanding fluid dynamics, chemical interactions, and related mechanisms is essential for controlling defects and ensuring structural integrity of fabricated parts.

The PBF-LB/M process is governed by multiple critical parameters, including laser power, spot diameter, scanning speed, powder layer thickness, shielding gas type, and gas flow rate. These variables collectively influence important phenomena such as phase formation, molten metal flow characteristics, surface tension effects, and Marangoni flow, all of which ultimately determine melt pool geometry and dimensions (Khairallah et al., 2016). To achieve optimal conditions, two essential criteria should primarily be fulfilled: (i) supplying adequate energy to fully melt both the deposited powder and underlying layer without inducing keyhole formation, and (ii) allowing sufficient interaction time for a stable melt pool to develop. If the supplied heat is inadequate, defects related to insufficient fusion zones appear, whereas excess heat input can result in the formation of keyhole porosity. Furthermore, excessively high scanning speeds can create melt pool instability, causing prominent spattering and balling phenomena because of the inadequate interaction time (Gor et al., 2021; Jing et al., 2020; K. Wei et al., 2017).

PBF-LB/M has been increasingly utilized in biomedical applications due to its capability to process bio-compatible alloys with precisely tailored properties (Gao et al., 2018; Sing et al., 2020). In particular, NiTi alloys have attracted significant attention in orthopaedic implants because of their remarkable superelasticity, permeability, stiffness, and damping characteristics, closely aligning with those required for human bone replacement. However, stringent control of structural and chemical properties is crucial for biomedical implants, where the impurity content must not exceed 500 ppm according to ASTM standards (Haberland et al., 2013). During additive manufacturing, impurity incorporation, particularly carbon, oxygen and nitrogen, can substantially affect the performance of bio-compatible components. Such impurities are especially critical in PBF-LB/M processes because their uptake intensifies at elevated temperatures (Hasib et al., 2021). One key method to mitigate this issue involves controlling the energy density applied during processing. Energy density, influenced directly by laser power and inversely by scanning speed, layer thickness, and hatch spacing (Meier & Haberland, n.d.), significantly affects the density of the final product as well as impurity absorption (Hasib et al., 2021). Higher energy inputs typically lead to greater material densification but simultaneously increase impurity levels, thereby necessitating careful optimization of processing parameters to balance mechanical properties and impurity control. Thus, optimizing process parameters to achieve minimal necessary energy density is vital, as energy density significantly influences the geometric fidelity of the fabricated component relative to its designed model.

PBF-LB/M utilizes fine metallic powders (~15–45 μm) to deposit extremely thin layers, thereby minimizing porosity arising from insufficient fusion (Gor et al., 2021). Although

employing higher laser powers can deepen the melt pool, this typically reduces dimensional precision. Consequently, PBF-LB/M is highly effective for fabricating small, intricate components, including aerospace parts, biomedical implants, and heat sinks. Nonetheless, due to the necessity of depositing very thin layers, production times increase significantly, restricting PBF-LB/M mainly to small-scale components. Alternatively, other energy sources, such as electron beams, can substitute lasers to enhance manufacturing speed.

2.4.1.2 Electron Beam Powder Bed Fusion (PBF-EB)

Electron Beam Powder Bed Fusion (PBF-EB) is another metal additive manufacturing method, utilizing electron beam energy to selectively melt metal powder layers (L. E. Murr et al., 2012). A schematic illustration of the PBF-EB process is presented in Figure 2-27. The electron beam system employed in PBF-EB closely resembles that of a scanning electron microscope. Similar to SEM, an electron gun provides the electron beam, and electromagnetic coils are utilized for precise beam focusing. Deflection coils control the path of the electron beam over the powder bed. Since electrons function as the energy source, the PBF-EB process must occur in a vacuum environment. Additionally, the powder supply mechanism in PBF-EB differs from that of PBF-LB techniques. Powder is stored in hoppers located within the vacuum chamber, and a raking blade distributes the powder evenly onto the base plate or the previously melted layer.

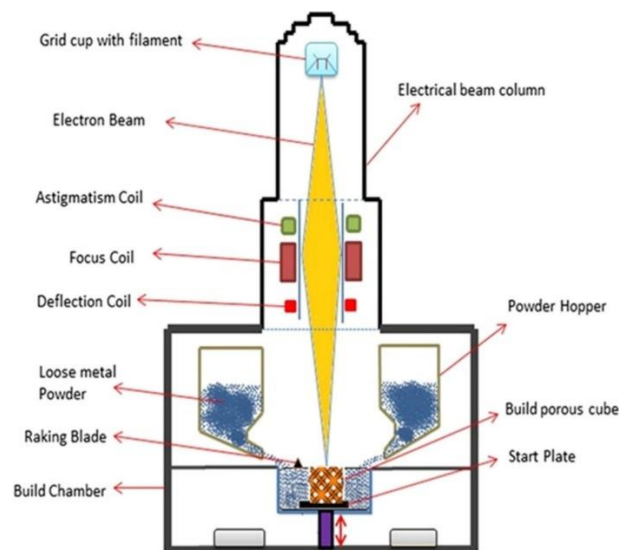


Figure 2-27 Schematic of PBF-EB (Moiduddin et al., 2017).

Electron beam energy plays a critical role as a processing parameter in PBF-EB, analogous to significance of laser power in the PBF-LB method. The electron beam parameters, such as beam power and spot size, can be precisely controlled to alter the electron beam characteristics (S. S. Al-Bermani et al., 2010). In PBF-EB, beam power is adjusted through beam current and accelerating voltage, whereas spot size is modulated by electromagnetic coils. Generally, titanium alloys processed by PBF-EB involve maximum beam powers around 3500 W and electron beam spot sizes in the range of 200–1000 μm (S. Liu et al., n.d.). In comparison, the maximum laser power and spot size in PBF-LB for titanium alloys are considerably lower, typically reaching 120 W and 30–150 μm , respectively (S. Liu et al., n.d.). Consequently, PBF-

EB has the capability to melt coarser powder particles and operate with thicker layers compared to PBF-LB. The typical layer thickness range for PBF-LB is about 30–60 μm , whereas PBF-EB commonly utilizes layers between 50–200 μm (Katz-Demyanetz et al., 2019). Nevertheless, the advantage of higher production rates in PBF-EB is counterbalanced by a trade-off in geometric precision and surface quality (Rafi et al., 2013). Components fabricated by PBF-EB exhibit lower spatial resolution and increased surface roughness. Additionally, sharp-angle features tend to suffer from pronounced stair-step artifacts due to the increased layer thickness in PBF-EB (Dowling et al., 2020).

Apart from the different energy sources employed, PBF-EB exhibits several other distinctions compared to PBF-LB/M. One significant characteristic unique to PBF-EB is the semi-sintering of powder particles, a step generally unnecessary in the PBF-LB/M process. Powder particles often accumulate electric charge upon interaction with the high-energy electron beam, causing smaller particles to become detached from the powder bed and form a particle cloud inside the vacuum chamber. To avoid this undesirable cloud formation, powder pre-sintering and pre-heating steps are conducted prior to the actual scanning process. This preliminary sintering reduces the need for extensive support structures; however, it also introduces challenges in removing residual semi-sintered powder following component fabrication. Consequently, pre-sintering adversely impacts the capability of PBF-EB to fabricate geometrically intricate features such as crevices, internal cooling channels, and lattice-based structures (Katz-Demyanetz et al., 2019). Another method to minimize powder charging involves increasing the internal vacuum chamber pressure. Typically, PBF-EB operations are conducted at chamber pressures around 10^{-2} Pa; this can be elevated to approximately 1Pa by introducing helium gas into the vacuum environment (Dowling et al., 2020).

2.4.2 Directed Energy Deposition (DED)

In metal additive manufacturing processes based on directed energy deposition (DED), both the feedstock and the energy input are simultaneously provided to produce a three-dimensional part (Selcuk, 2011). Figure 2-28 presents a schematic illustration of the DED method. Unlike powder bed fusion, DED injects the feedstock material directly onto a substrate rather than spreading it in a powder bed. The supplied energy melts this injected feedstock on the substrate, after which it solidifies to form the intended object. Various heat sources can be utilized, including a laser beam (F. Q. Liu et al., 2020), electron beam (Y. H. Jang et al., 2018), or electric arc (Duarte et al., 2022), while the feedstock itself can be supplied as powder (A. Singh et al., 2020) or wire (B. T. Gibson et al., 2020). Depending on the specific combination of energy source and feedstock material, DED is referred to by different terminologies, including direct metal deposition (Pinkerton, 2015) or laser metal deposition (K. Zhang et al., 2014), electron beam additive manufacturing (Edwards et al., 2013), wire and arc additive manufacturing (Rodrigues et al., 2019), or rapid plasma deposition (Pratheesh Kumar et al., 2021). In many aspects, DED closely resembles metal inert gas (MIG) welding, particularly regarding the simultaneous feedstock delivery and the use of shielding gas flow protecting the molten pool. Specifically, in laser-based DED, a nozzle delivers metal powder along with shielding gas onto the substrate surface. At this location, a focused laser beam melts the metal

powder, and the building platform moves following instructions derived from a CAD model to achieve selective deposition. The desired object is thus built layer-by-layer through repeated deposition and subsequent solidification of the molten powder layers (T. S. Jang et al., 2020). In some DED configurations, instead of the build platform moving, the deposition nozzle itself is maneuvered by a robotic arm while the substrate remains stationary (Herzog et al., 2016).

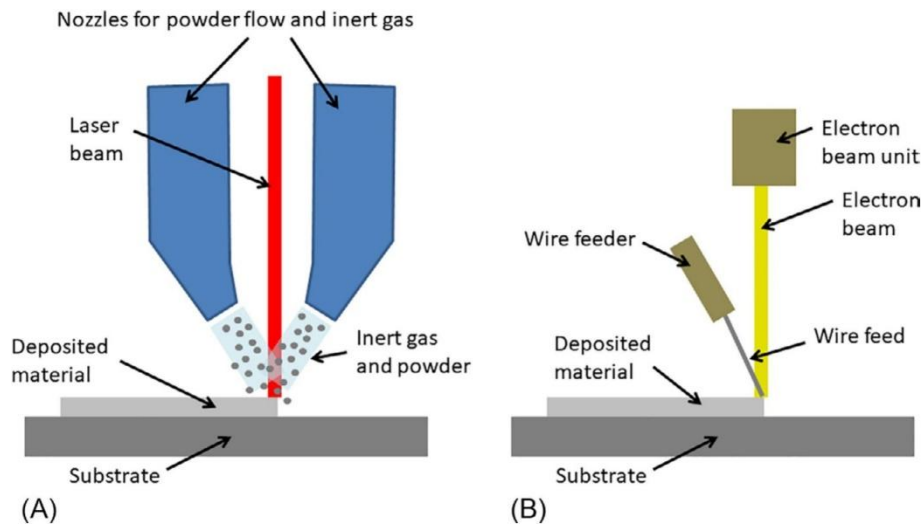


Figure 2-28 Schematic representation of the directed energy deposition (DED) additive manufacturing process: (a) Powder feedstock with laser beam heat source, (b) Wire feedstock with electron beam heat source (Sing et al., 2020).

High-speed imaging techniques have been employed to track the position of the build specimen during fabrication. Moreover, melt pool temperatures and powder delivery rates are continuously monitored using an infrared (IR) pyrometer and real-time sensing devices, respectively. Within a closed-loop control system, these real-time measurements are systematically acquired and analysed, enabling the generation of feedback signals for process adjustments. Such feedback is subsequently utilized to optimize fabrication conditions. Specifically, nozzle positioning, melt pool stability, and deposition consistency are enhanced by adapting parameters such as nozzle movement and powder feed characteristics. Key experimental parameters informed by these sensor data include nozzle size, nozzle height, and powder flow characteristics, encompassing powder size distribution and morphology (Gao et al., 2018).

In DED processes, the selection of parameters including laser power, powder feeding rate, and deposition speed directly influences the melt pool shape, resulting surface roughness, and mechanical performance (Y. Li et al., 2017). Specifically, increased path velocity reduces melt pool dimensions due to shorter laser-powder interaction time, while enhancing powder feed rate and laser power enlarges the melt pool (Sampson et al., 2021). Typically, DED utilizes relatively coarser powder particles and employs higher energy densities than those common to PBF. Unlike the PBF method, where the component remains embedded in a powder bed, DED-produced parts experience quicker cooling due to the exposed deposition surface. This enables higher build speeds and the capability to manufacture larger components using DED.

Nevertheless, accelerated deposition rates often compromise surface quality, leading to increased roughness and reduced dimensional accuracy. Consequently, additional post-processing steps are required to achieve acceptable surface finish standards.

DED is recognized for its effectiveness in fabricating medium-sized metal components, achieving production speeds roughly ten times greater and costs approximately five times lower compared to PBF methods (Optomec Inc., 2018). This method supports various metal powders or their mixtures, as powders are delivered externally during fabrication, allowing simultaneous or sequential feeding of different powders (Keshavarz et al., 2021; Optomec Inc., 2018). Consequently, DED enables the creation of advanced materials and tailored alloys for specific applications, including biocompatible and antimicrobial alloys (J. D. Avila et al., 2018), porous metallic implants for bone replacement (W. Xue et al., 2007), and specialized dental materials (Revilla-León et al., 2020). Moreover, versatility of DED in handling diverse powder materials or combinations enhances its attractiveness for advanced biomedical applications. Due to its unique processing characteristics, DED also excels in repairing and manufacturing intricate metal components that might otherwise pose challenges with traditional manufacturing techniques, demonstrating particular advantages in cost and speed compared to PBF (Optomec Inc., 2018). Specifically, DED can produce medium-scale parts approximately ten times faster and at one-fifth the cost compared to PBF techniques (Optomec Inc., 2018). Additionally, the externally supplied powder in DED allows manufacturing complex or functionally graded components, widening its applicability in demanding industries. For instance, DED has been effectively utilized to repair high-value components, such as turbine blades and aerospace structures, which are otherwise difficult to restore with conventional manufacturing processes.

2.4.2.1 Process Parameters

The selection of appropriate DED process parameters typically relies on material type, geometry of the component, and specific application-driven criteria, such as acceptable levels of porosity and surface roughness. The key parameters influencing the energy input include beam power and beam spot size, while deposition-oriented variables encompass powder feeding and deposition strategies. Moreover, the powder characteristics—such as particle morphology, particle size distribution, and surface quality—material properties including thermal conductivity, chemical composition, viscosity, reflectivity, and surface tension, along with environmental factors like vacuum conditions, inert gas atmosphere, and gas flow rates, collectively influence melt pool behaviour. As in other additive manufacturing methods, these parameters are interconnected, thus complicating their generalization; for example, energy input adjustments, such as increasing beam power, often require corresponding modifications in scanning speed to achieve desired outcomes (I. Gibson et al., 2015). To address such complexities, a closed-loop feedback control system is commonly integrated into additive manufacturing monitoring setups to dynamically regulate individual parameters, maintain consistency, and ensure the final quality of the built components (Z. jue Tang et al., 2020). Thus, systematic investigation into each individual processing parameter is required to gain a

comprehensive understanding of their effects on melt pool dynamics, microstructural evolution, mechanical properties, and the formation of defects.

The main parameters influencing melt pool optimization include beam power, scanning speed, and feedstock flow rate (Bax et al., 2018). Particularly in DED processes, input energy density plays an essential role, as it determines whether the feedstock melts completely. Achieving complete melting relies heavily on input energy density, which has been highlighted as a critical factor. Therefore, energy density should be carefully controlled and monitored. To ensure complete melting of feedstock, energy density can be expressed as a comparative parameter. For instance, it is often necessary either to increase the laser power or to reduce scanning speed or feedstock rate to maintain a suitable energy density; otherwise, higher scanning speeds or powder flow rates can reduce melting efficiency (Traxel et al., 2020). Notably, a previous study has defined that energy density directly ensures the complete melting of powder feedstock in the DED process as it is indicative of the balance among these parameters. Increasing the powder deposition rate can generally be accomplished through higher material flow rates combined with elevated laser power, assuming all other processing parameters remain constant (Shim et al., 2016). Nevertheless, it should be considered that increasing laser power can lead to larger thermal gradients, consequently generating increased residual stresses (Bian et al., 2020). As a result, higher residual stresses can trigger undesirable effects such as component distortion or even cracking. For instance, numerical modelling of the DED process for Inconel 718 indicated that increasing laser power results in wider and deeper melt pools (Lee et al., n.d.). This broader melt pool formation occurs due to higher heat input and enhanced material flow, though it does not significantly alter the deposition height.

In powder-based DED, scanning speed refers to the movement speed of the deposition head during powder deposition. Apart from powder flow rate, the scanning speed serves as a control parameter influencing the quantity of material introduced into the melt pool (Svetlizky et al., 2021). It dictates the residence time available for interaction between the laser beam and the supplied material. This residence time significantly impacts both solidification characteristics and the resulting microstructural development (Manvatkar et al., 2015). Moreover, scanning speed also influences material flow dynamics, such as surface tension effects and Marangoni convection (Z. Zhao et al., 2021).

Processing parameters strongly rely on the characteristics of the materials involved. Figure 2-29 illustrates the optimal processing conditions and the associated likelihood of defect formation across different alloy systems. At very low powder feed rates combined with high linear heat inputs, excessive energy density promotes the formation of a keyhole-shaped melt pool. On the other hand, when the powder feed rate is increased and linear heat input is reduced, the resulting energy density decreases significantly. Under these conditions, the supplied energy is insufficient to achieve complete melting of the powder particles, leading to incomplete fusion defects. Additionally, a mid-porosity region develops when high linear heat input is simultaneously paired with a high powder feed rate (Dass & Moridi, 2019).

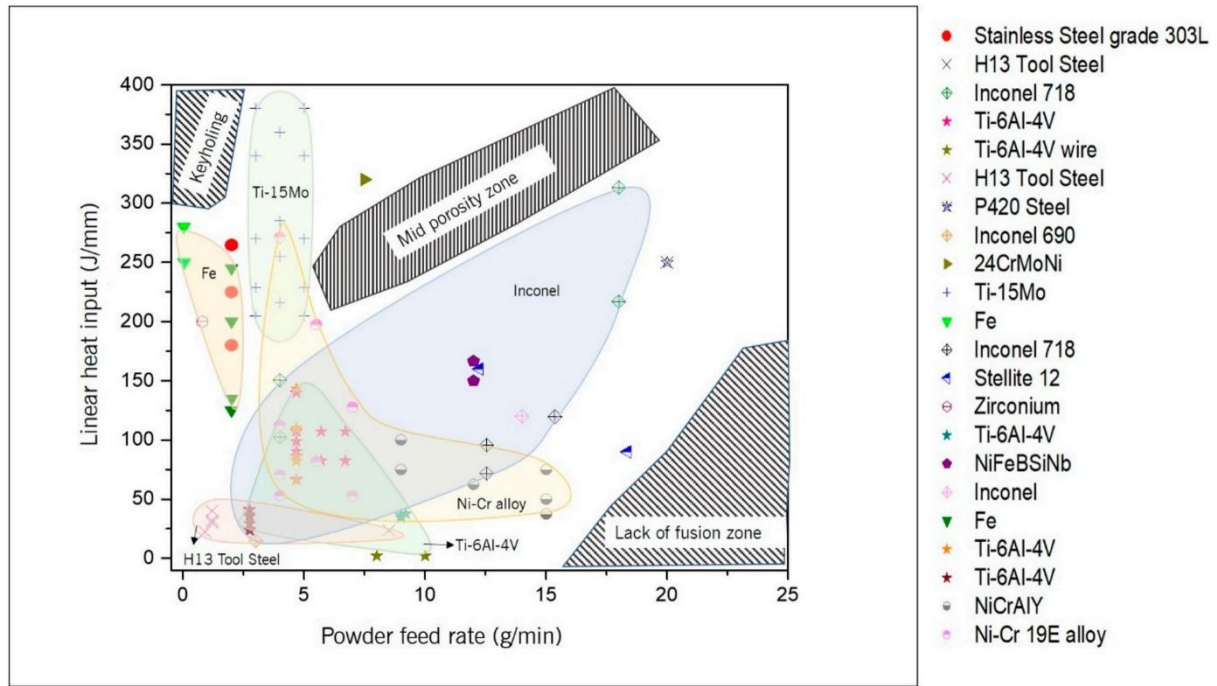


Figure 2-29 Optimal processing parameters and potential defect formation in the DED process (Dass & Moridi, 2019).

2.4.3 Microstructure Control During PBF-LB/M

2.4.3.1 PBF-LB/M Process Optimization

2.4.3.1.1 Parameters

Optimising the processing parameters is crucial for managing the microstructure in PBF-LB/M (K. Liu et al., 2022). However, most current optimisation methods rely on trial-and-error experimentation and do not yet provide a thorough theoretical basis tailored to PBF-LB/M microstructure control. The growth restriction factor (Easton & StJohn, 1999), Q , extensively used in conventional casting, has demonstrated effectiveness in grain refinement by analysing the effects of parameters or composition. It has also proved invaluable for understanding grain refinement during alloy solidification, thus underscoring its significance for the quality of cast and wrought alloys (Greer et al., 2000). The growth restriction factor Q characterises the principal factors governing the development of undercooling, while the balance between nucleation and growth ultimately dictates the final grain size (Schmid-Fetzer & Kozlov, 2011). As shown in Figure 2-30, lower G/R ratios favour equiaxed dendritic structures, whilst higher $G \times R$ values lead to smaller grain sizes. Parameters such as laser power, scanning speed, hatch spacing, and layer thickness influence the temperature gradient and cooling rates, thus affecting crystal morphology and phase transition.

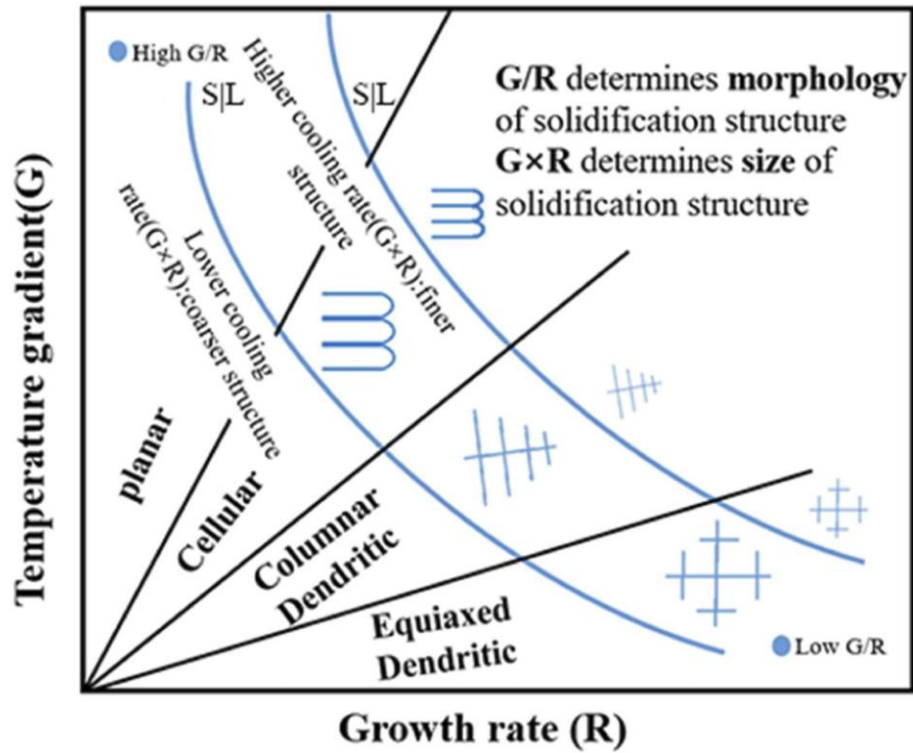


Figure 2-30 Influence of temperature gradient (G) and growth rate (R) on grain size and morphology. Labels S and L denote solid and liquid phases, respectively (Jersey et al., 2019).

In-situ precipitation, achieved by optimising scanning parameters, has been employed to induce nano-precipitates during additive manufacturing. This method has demonstrated promising outcomes for simultaneously enhancing both strength and ductility. For instance, Fe19Ni5Ti steel was specifically tailored for laser additive manufacturing through the local control of nanoprecipitation and martensitic transformation (Kürnsteiner et al., 2020). The as-built steel was in-situ hardened by NiTi nanoprecipitation, featuring alternating soft (precipitate-free) and hard (precipitate-rich) layers, attaining a tensile strength of 1.3 GPa and 10 % elongation. Guo et al. proposed a phase-transformation-guided approach for microstructure control during PBF-LB/M of 17-4PH steel (Q. Guo et al., 2022). By managing scanning parameters, they minimised δ -ferrite formation yet facilitated austenitisation. Overall, a thorough understanding of the interplay among processing parameters—such as laser power, scanning speed, layer thickness, and hatch spacing—and their impact on temperature gradients and cooling rates is vital for optimising microstructure in PBF-LB/M. Establishing theoretical frameworks and integrating phase transformation behaviour are essential steps towards achieving precise regulation of microstructural characteristics.

2.4.3.2 Scanning Strategy

In addition to individual parameters, the scanning strategies employed in PBF-LB/M exert a considerable impact on the resulting microstructure (Geiger et al., 2016). By adjusting these strategies, one can refine the thermal gradient, solidification rate, and heat flux, thereby obtaining the intended microstructural characteristics. Several principal elements of scanning strategy are as follows.

2.4.3.2.1 Scanning Patterns

Multiple scanning patterns are employed in PBF-LB/M, including stripes, chessboard/island, spiral paths, and fractal strategies (Catchpole-Smith et al., 2017), as shown in Figure 2-31. Stripe scanning strategies, such as unidirectional and bidirectional (zigzag), are efficient but may produce a layered or ‘staircase’ surface finish. These patterns typically foster columnar grain growth along the build direction, leading to a pronounced texture (J. Xu et al., 2023). Carter et al. verified that the back-and-forth (bidirectional) scanning pattern generated a uniformly columnar structure along the building direction when processing nickel-based superalloys via PBF-LB/M (Carter et al., 2014). Marcus et al. likewise observed that scanning patterns featuring a slight adjustment in the direction of the laser vector favour columnar grain growth, creating a stronger texture and fewer high-angle grain boundaries (Lam et al., 2022). However, this simplified scanning mode is less appealing for fabricating distinctive microstructures. More intricate scanning approaches such as chessboard, spiral, and fractal patterns can modify the thermal field—particularly the maximum temperature gradient—and diminish residual stresses, thereby enabling the formation of the desired microstructure with excellent properties. Liu et al. examined various scanning strategies for Ti6Al4V and noted that the hexagon pattern produced columnar primary β grains aligned with the build direction, whereas the chessboard pattern was characterised by equiaxed primary β grains (J. Liu et al., 2022). Catchpole-Smith et al. found that fractal scanning patterns can enhance part density in comparison to island scanning, offering a novel method for thermal management and crack suppression in PBF-LB/M (Catchpole-Smith et al., 2017). In general, chess scanning patterns tend to yield a cube texture (J. Liu et al., 2022; Thijs et al., 2013), while the texture produced by bidirectional scanning strategies also depends on the interlayer rotational angle (Geiger et al., 2016).

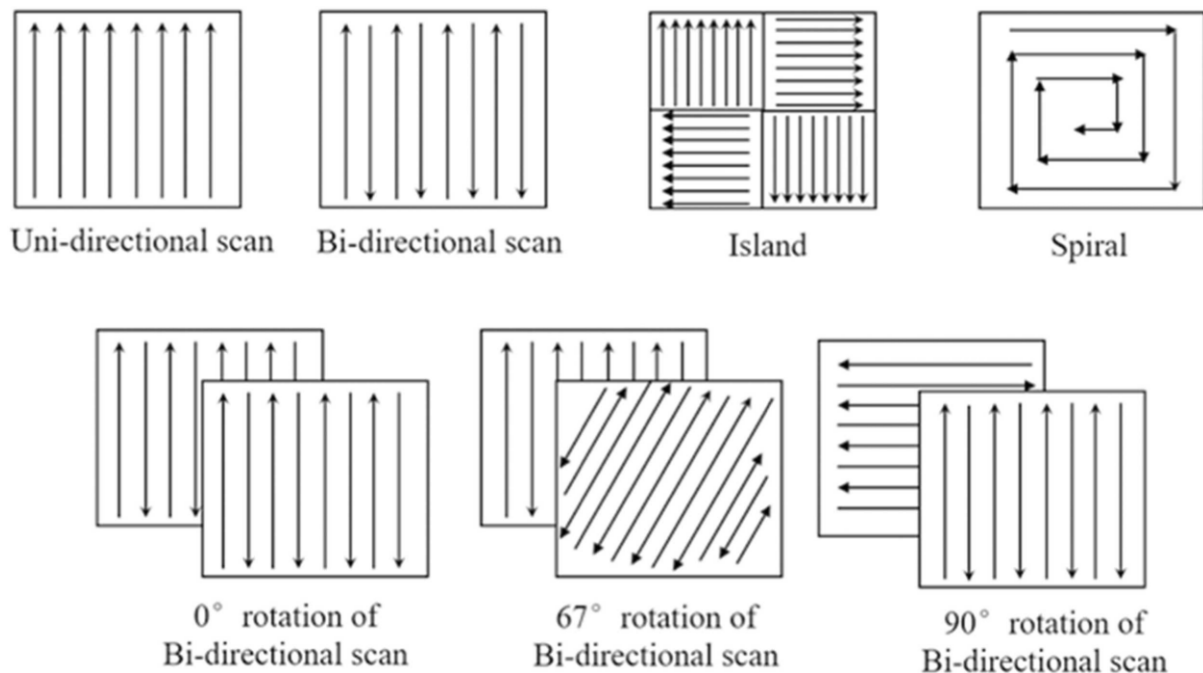


Figure 2-31 Schematic illustration of various laser scanning patterns utilized in PBF-LB/M (Catchpole-Smith et al., 2017).

2.4.3.2.2 Interlayer Rotational Angle

The angle of rotation between consecutive layers plays a substantial role in microstructure control. Rapid changes in the thermal gradient can interrupt epitaxial growth and encourage the nucleation of fresh grain orientations. By adjusting the rotational angle, one can steer both the grain growth direction and the resulting microstructure. Hatakeyama et al. reported that, when producing 9Cr-1Mo steel by means of PBF-LB/M, a more pronounced cubic texture emerged with a 90° interlayer rotational angle, compared with 67° (Hatakeyama et al., 2023). This is because an angle of 67° produces a larger heat-affected zone than 90° , thereby favouring the formation of equiaxed grains and hindering the epitaxial growth of columnar grains.

Sofinowski et al. employed three bidirectional scanning approaches featuring different interlayer rotational angles during the PBF-LB/M of 316L stainless steel (Sofinowski et al., 2021). As illustrated in Figure 2-32 (I), these scanning patterns are referred to as Helicoidal, LEGO Brick, and Embedded Cylinder, respectively. As depicted in Figure 2-32 (II-IV), the use of these strategies enabled the production of controllable crystallographic textures. Rotating the scanning direction modifies the thermal gradient, which in turn results in distinct orientations of grain growth.

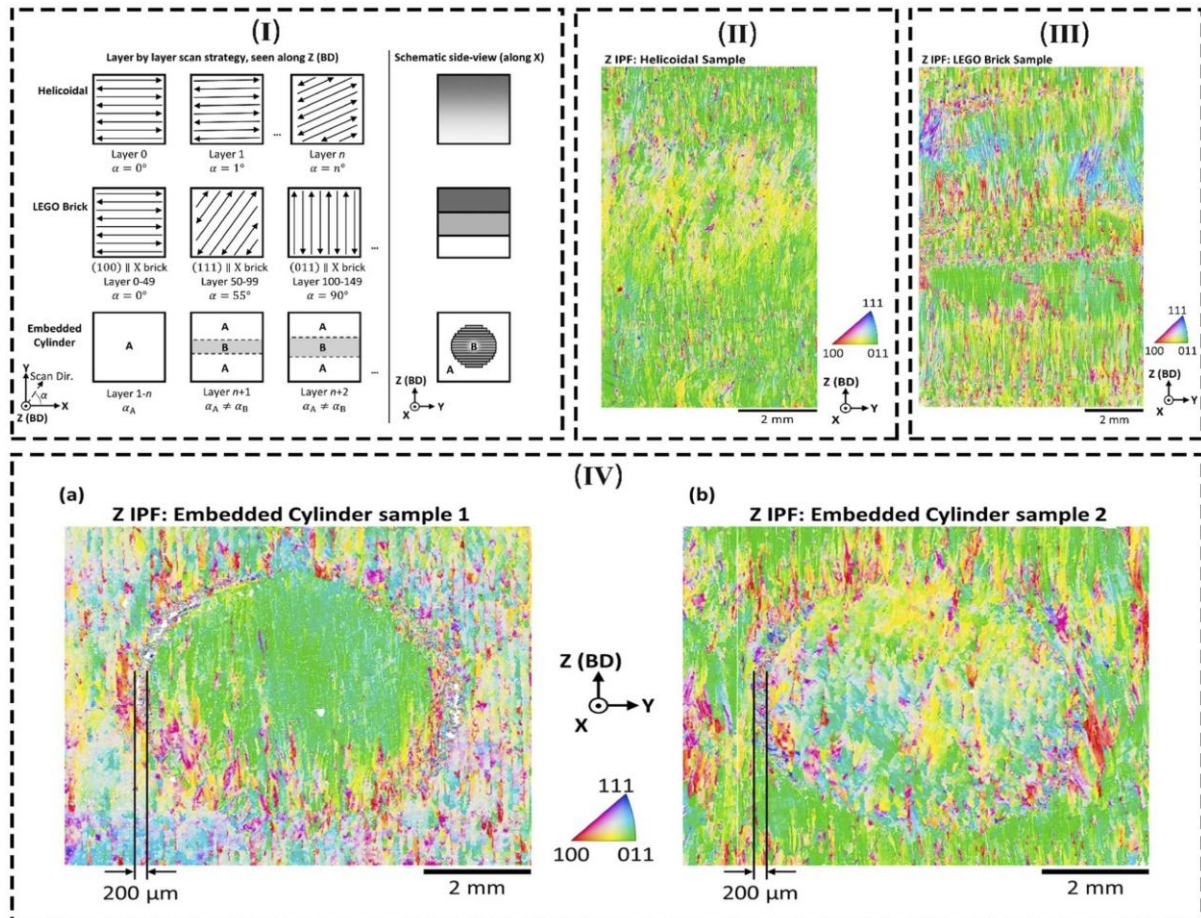


Figure 2-32 (I) Illustrations of the Helicoidal, LEGO Brick, and Embedded Cylinder scanning patterns. Panels (II), (III), and (IV) present the corresponding inverse pole figure (IPF) maps associated with each scanning strategy (Sofinowski et al., 2021).

2.4.3.2.3 Re-Melting

During PBF-LB/M, re-melting refers to melting layers that have already solidified. This approach aids in homogenising chemistry, lowering thermal stress, and preventing cracks (Chmielewska et al., 2022). As illustrated in Figure 2-33 (I), the layer-by-layer re-melting process noticeably enlarges the melt pool (Q. Shi et al., 2022). Zhou et al. utilised an in-situ re-melting strategy to manage molten pool geometry in the PBF-LB/M of a NiCoCr medium entropy alloy (K. Zhou et al., 2023). Their findings reveal that re-melting promotes densification and grain refinement without diminishing the heterogeneous microstructure. Moreover, this process creates a distinctive crystallographic lamellar texture and elevates dislocation density, thereby markedly boosting strength without sacrificing ductility. Zhou et al. examined the microstructure evolution of AlSi10Mg alloy using layer-by-layer re-melting during PBF-LB/M (J. Zhou et al., 2021). As indicated in Figure 2-33 (II), laser re-melting refines grains, heightens the crystallographic texture, and intensifies anisotropy. The enhanced temperature gradient and cooling rate during re-melting facilitate the removal of stray grains and dendrites, producing refined grain structures with stronger crystallographic textures. As shown in Figure 2-33 (III (g and h)), re-melting can remove stray grains and dendrites from the top of the melt pool and amplify heat input. According to Figure 2-33 (III (i and j)), robust texture may be attained during re-melting by selecting suitable parameters (W. Shao et al., 2022). In Figure 2-33 (IV), Yang et al. observed that a narrow re-melting hatch spacing converts the crystallographic orientation from a fibre texture to a cubic texture, while the overall texture intensity grows as hatch spacing decreases when processing 316 L via PBF-LB/M (Y. Yang et al., 2020).

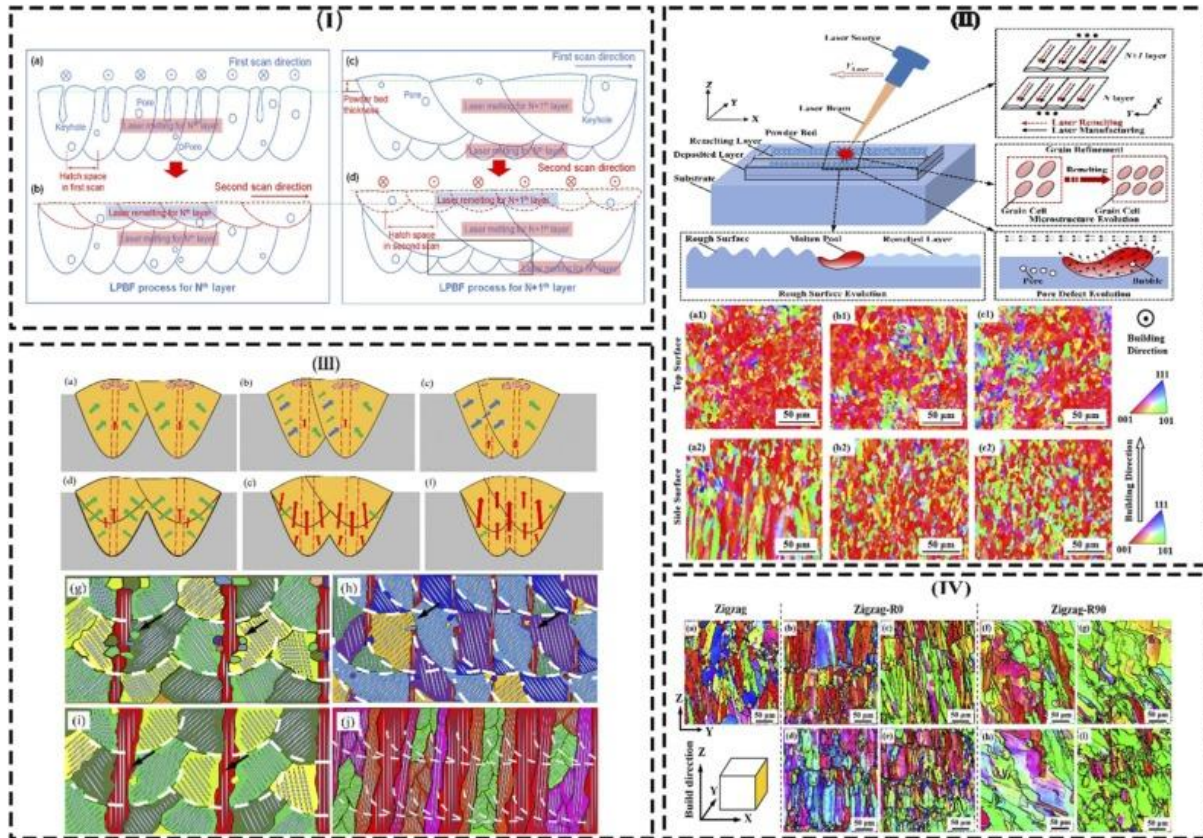


Figure 2-33 A schematic diagram illustrating the laser re-melting process: (I) Shows the melt pool structure for laser melting and re-melting strategies in PBF-LB/M (Q. Shi et al., 2022). (II) Provides a schematic overview and inverse pole figure (IPF) maps of laser re-melting in PBF-LB/M (J. Zhou et al., 2021). (III) Demonstrates how hatch spacing overlaps and laser re-melting affect growth texture, where (a, b, c, g, h) display the influence of hatch spacing, and (d, e, f, i, j) depict dendrite growth with re-melting (W. Shao et al., 2022). (IV) Depicts the grain structure of samples fabricated via PBF-LB/M with different scanning approaches: (a) zigzag, (b–e) zigzag re-melting without interlayer rotation, and (f–i) zigzag re-melting with a 90° interlayer rotation. Hatch spacings are 30 μm in (b, f), 20 μm in (c, g), 15 μm in (d, h), and 10 μm in (e, i) (Y. Yang et al., 2020).

2.4.3.3 Effect of Baseplate Used

2.4.3.3.1 Crystallography

The substrate material and its structure, as well as the crystallography of the baseplate, exert a notable influence on solidification behaviour and the resulting microstructure in PBF-LB/M. If the substrate composition matches that of the part being built, crystal nucleation is more readily achieved because they share the same crystal structure, thereby lowering nucleation energy. In the case of single-crystal substrates, columnar grains propagate epitaxially along particular directions (for example, $\langle 001 \rangle$ in face-centred cubic crystals) owing to single-crystal seeds (L. Wang et al., 2015). Nonetheless, the preferred growth direction and thermal gradient can alter the dendrite growth pathway, producing both oriented and mis-oriented growth (J. Liu & To, 2017). These oriented and mis-oriented dendrites continue their growth until the columnar-to-equiaxed transition occurs near the top of the melt pool (J. C. Guo et al., 2019), as depicted in Figure 2-34 (a). It is noteworthy that both types of dendrites exhibit the same

crystallographic orientation but may follow distinct growth directions, as illustrated in Figure 2-34 (a) and (c).

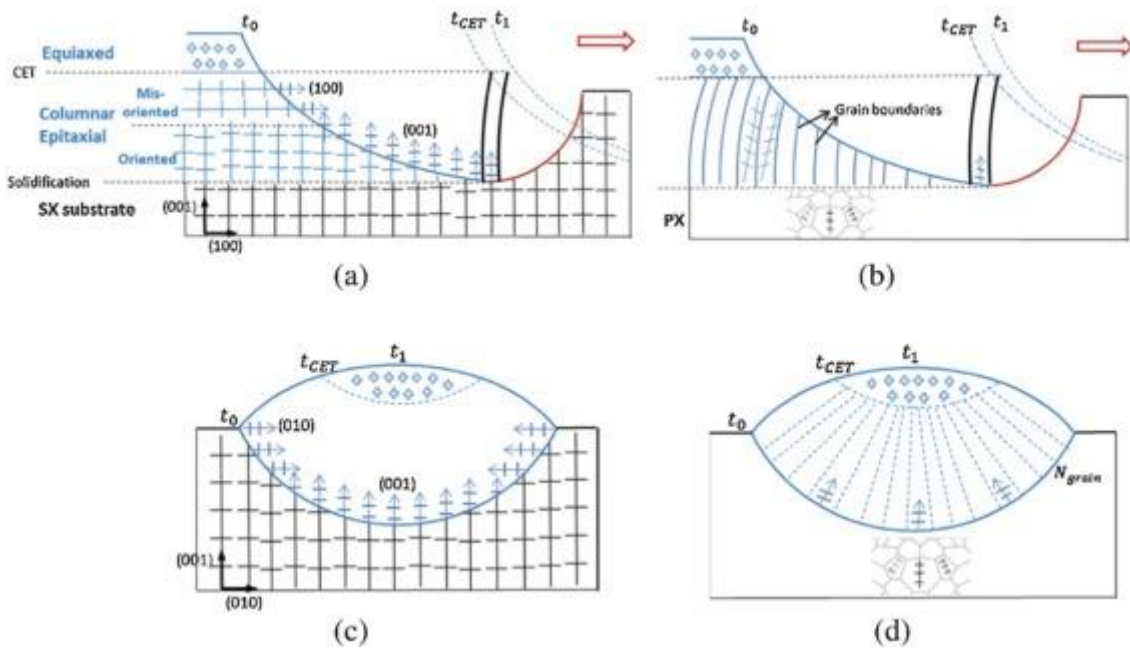


Figure 2-34 Schematic illustration of how varying substrate materials and crystallographic orientations affect the crystal growth direction. Figures (a) and (c) depict the columnar epitaxial growth arising from single-crystal substrates, whereas (b) and (d) display the transverse cross-section at the initial stage of solidification of a polycrystalline substrate (G. Liu et al., 2021).

In polycrystalline substrates, dendrites can form along multiple crystallographic orientations in different regions. Due to the Walton-Chalmers model (Rappaz & Gandin, 1993), those that are favourably oriented outgrow the others (Figure 2-34 (b)), continuing to develop until they encounter the equiaxed zone via CET (Figure 2-34 (d)). In contrast to single-crystal baseplates, where the columnar zone is monocrystalline, the columnar region that forms on a polycrystalline baseplate remains polycrystalline. Liu et al. proposed a mathematical model to anticipate crystal growth during laser powder deposition of the nickel-based superalloy Rene N5 (Z. Liu & Qi, 2015). According to their findings, changes in the crystallographic orientation of substrate within the XZ section (where Z is the build direction and X the scanning direction) predominantly affect the CET position. Conversely, in the YZ section, the substrate crystallographic orientation primarily governs the competitiveness of the preferred growth direction. Ishimoto et al. investigated crystal texture stability during PBF-LB/M, concluding that it is largely determined by the orientation of substrate (Ishimoto et al., 2021). By using a single-crystal seed substrate, a single-crystal region can be maintained under the PBF-LB/M process, thus providing a means of designing and steering microstructure evolution in PBF-LB/M (Z. Liu & Qi, 2015).

2.4.3.3.2 *Baseplate Temperature*

In directed energy deposition, it is a standard practice to utilise substrate preheating to alleviate cracking, which is generally attributed to rapid cooling (Zarini et al., 2014; S. Zhou, Huang, et al., 2008; S. Zhou, Zeng, et al., 2008). However, in laser powder bed fusion, industrial PBF-LB/M systems typically restrict preheating to roughly 200°C. This comparatively low temperature is often adopted to minimise porosity or cracking by stabilising the melt pool and reducing cooling rates (Karthik et al., 2022). Furthermore, the temperature chosen for baseplate preheating, alongside the subsequent cooling strategy, influences the temperature gradient, cooling rate, and solidification front growth behaviour during PBF-LB/M (Schmitt et al., 2020), ultimately affecting the resultant microstructure (R. Mertens et al., 2018).

Substrate preheating has also been employed to induce phase transformations. For example, Raffei et al. examined the precipitates in an AA2099 Al-Cu-Li alloy, both with and without baseplate preheating during PBF-LB/M (Raffei et al., 2020). They observed that no precipitates formed in the as-built condition without preheating, whereas two main phases, T1 (Al_2CuLi) and TB ($\text{Al}_{7.5}\text{Cu}_4\text{Li}$), emerged when the baseplate was preheated to 320°C and 500°C, thereby enhancing the as-built strength of the sample. Although they did not reduce cracking in PBF-LB/M through this method, their work demonstrates a pathway for achieving precipitation of strengthening phases via baseplate preheating. Moreover, baseplate preheating can lead to microstructural alterations owing to tempering effects (Demir & Previtali, 2017), such as precipitation in Al7075 (Montero Sistiaga et al., 2016), austenite–martensite transformation in H13 tool steel (R. Mertens et al., 2016), and grain coarsening in Hastelloy X (Tomus et al., 2017), all observed at temperatures below 400 °C. Riener et al. investigated the impact of enhanced preheating on the microstructure of EN AW 6182 aluminium alloy during PBF-LB/M (Riener et al., 2022). Their findings indicated that, at preheating temperatures of 500°C, the resulting microstructure largely comprised equiaxed grains, as compared to columnar grains formed without baseplate preheating. Liu et al. researched the effects of baseplate preheating and precooling on single-crystal growth in laser powder deposition (Z. Liu & Wang, 2018). They noted that the preset temperature of the substrate adversely influenced melt pool geometry but strongly affected the transition from columnar to equiaxed grains, as well as primary dendrite arm spacing. Specifically, they identified that at temperatures below 90°C, any stray grains at the top of the melt pool could be fully remelted during layer-by-layer printing in laser powder deposition, thereby promoting epitaxial columnar grain growth. Additionally, they observed that baseplate precooling further supported the epitaxial growth of columnar grains.

In summary, baseplate parameters—encompassing substrate material, structure, temperature, and build angle—are pivotal in determining the microstructure evolved during PBF-LB/M. By understanding and optimising these parameters, it becomes possible to govern and modify the final microstructure, achieving the desired material properties in manufactured components.

2.4.3.4 Effect of Laser Beam

2.4.3.4.1 Intensity Profile of Laser Beam

The spatial distribution of laser power, referred to as the laser beam intensity profile, can be modified to produce particular microstructural outcomes (Y. Zhao et al., 2023). Various intensity profiles—such as Gaussian, flat-top, and doughnut—deliver distinct energy distributions into the melt pool. Of these options, the Gaussian profile is the most frequently employed in PBF-LB/M, characterised by a peak intensity at the beam's centre that diminishes towards the edges, as shown in Figure 2-35 (I(a)). In this configuration, the laser intensity follows a Gaussian distribution. When interacting with metallic powder, the Gaussian-profile laser gives rise to a comparatively narrow heat-affected zone, prompting columnar grain growth along the periphery of the melt pool. However, this narrow melt pool also amplifies Marangoni convection, which may in turn lead to defects such as keyhole porosity.

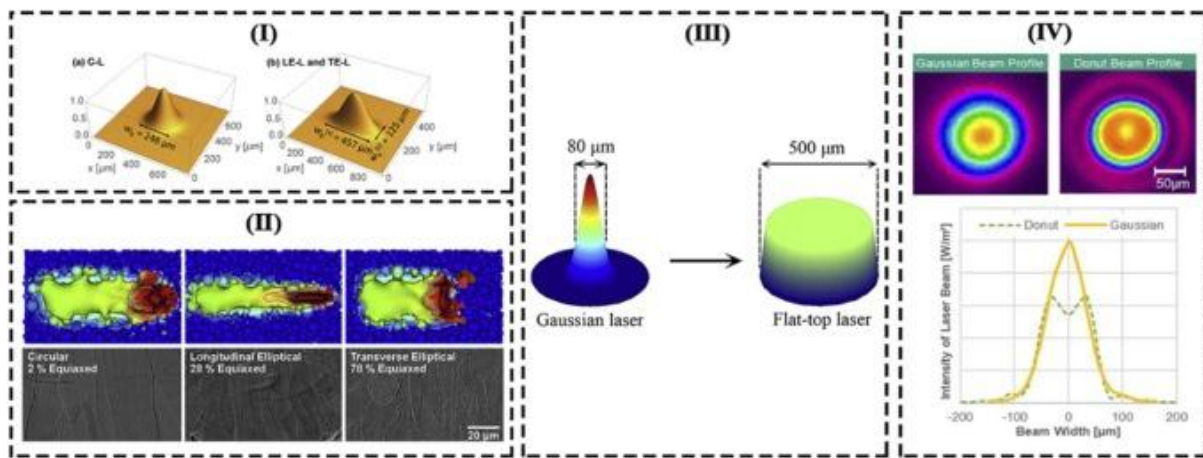


Figure 2-35 Laser beam intensity profiles employed in PBF-LB/M. (I) and (II) show the Gaussian profile and elliptical beam shapes—longitudinal elliptical (LE) and transverse elliptical (TE)—along with the resulting microstructure (Roehling et al., 2017). (III) compares the Gaussian and flat-top laser profiles (Yuan et al., 2022), while (IV) illustrates the Gaussian and doughnut laser profiles (Gerstgrasser et al., 2021b).

The flat-top profile (Figure 2-35 (III)) is characterised by a relatively uniform intensity distribution across the beam, forming a flat plateau and a sharp decline at its edges. This homogeneous energy distribution in the melt pool supports a flatter melt pool shape and can promote epitaxial grain growth, resulting in columnar dendrites and single crystals. In the PBF-LB/M process, Yuan et al. compared the microstructures produced by a flat-top laser with a large spot size and a Gaussian laser when fabricating Inconel 718 (Yuan et al., 2022). They found that the flat-top laser was more conducive to epitaxial columnar grain growth. This occurs because the melt pool generated by a flat-top laser has a higher width-to-depth ratio and a flatter bottom boundary, as also reported by Jodi et al. (Jodi et al., 2023) and Liu et al. (Y. Liu et al., 2021). In contrast to the intense Marangoni flow commonly encountered under Gaussian beams, the flow in a flat-top-induced melt pool is more moderate, thereby facilitating epitaxial growth of columnar grains. Consequently, the flat-top laser is frequently employed to form single crystals during PBF-LB/M (Jodi et al., 2023; Y. Liu et al., 2021). The doughnut

profile (Figure 2-35 (IV)) features minimal or no intensity at the beam centre, surrounded by a ring of higher intensity. This configuration can be achieved using vortex beams or beam-shaping optics and proves advantageous for scenarios requiring specific heat distribution—such as establishing temperature gradients for microstructural control or reducing thermal stresses. Cloots et al. compared a Gaussian laser and a doughnut laser in the PBF-LB/M of IN738LC and observed that laser type had little influence on texture, whereas scanning strategy had a pronounced effect (Cloots et al., 2016).

Elliptical beam profiles, including longitudinal elliptical (LE) and transverse elliptical (TE) variants, can yield distinct microstructures, as illustrated in Figure 2-35 (I-II). The TE profile often promotes a more uniform microstructure composed of equiaxed grains, whereas the LE profile encourages columnar epitaxial growth and a stronger texture. Roehling et al. (Roehling et al., 2020) and Matthews et al. (Matthews et al., 2018) showed that a TE beam profile favours smaller equiaxed grains with random orientations in PBF-LB/M. Shi et al. also found that a melt pool generated by a TE beam is shorter, wider, and shallower than that induced by a Gaussian beam (R. Shi et al., 2020). In contrast, the LE beam produces the strongest columnar texture, followed by the Gaussian beam and then the TE beam. Because the transverse elliptical energy distribution leads to a higher nucleation rate, the resulting microstructure is typically equiaxed or a blend of columnar and equiaxed grains, which diminishes crystallographic alignment and, in turn, reduces the texture index (Roehling et al., 2020).

2.4.3.4.2 Diameter and Focus Shift of Laser Beam

The diameter of the laser beam can be adjusted to control the size and shape of the melt pool. A smaller beam diameter usually produces a narrower and deeper melt pool, encouraging the growth of equiaxed grains (McLouth et al., 2018). In contrast, a larger beam diameter typically leads to a wider and shallower melt pool, which favours the formation of columnar grains. By fine-tuning the laser beam diameter, different melt pool morphologies can be achieved, and cracks can be alleviated. Sow et al. compared the energy distribution and microstructural evolution using lasers with varying diameters (Sow et al., 2020). Their findings indicate that a small beam diameter results in melt pools prone to splashing and instability, whereas a large beam diameter yields a more stable melt pool with longer columnar grains.

Altering the focal plane of the laser beam, often termed laser focus shift, offers a way to modify the aspect ratio (width/depth) of melt pools, as depicted in Figure 2-36. Adjusting the focus shift changes the laser spot size, thereby influencing both cooling rate and solidification behaviour. This approach can be employed to encourage either columnar or equiaxed grain development. A high melt pool aspect ratio leads to a flattened melt pool geometry, which promotes columnar dendrite growth. When the focal plane shifts away from the waist radius, the laser diameter increases while power intensity decreases, facilitating columnar dendrite formation in the solidification structure. Moving the focal plane also broadens the re-melted equiaxed grains in the overlapping region and induces columnar grains with a preferred orientation. In the PBF-LB/M of CM247LC, Gerstgrasser et al. calibrated the laser focal plane and observed that enlarging the focal diameter mitigates cracks and achieves a pronounced

texture (Gerstgrasser et al., 2021a). McLouth et al. further reported that adjusting the laser focus considerably enlarges the spot size and alters the power density (McLouth et al., 2018).

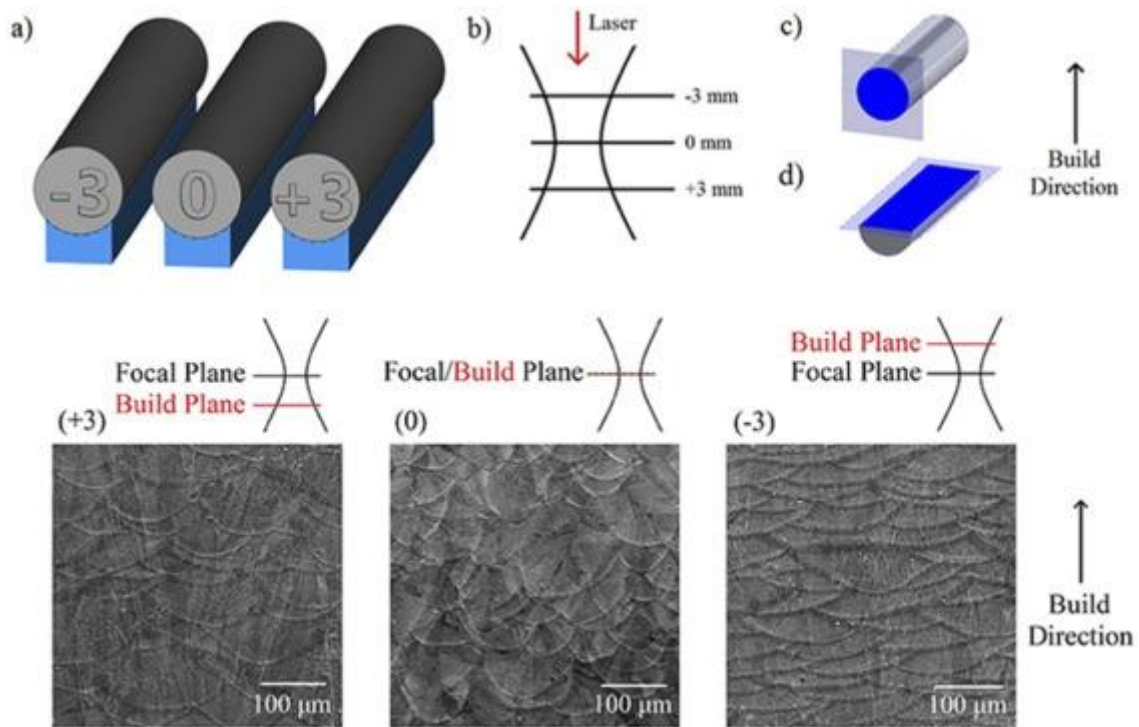


Figure 2-36 Laser focus shifts and their corresponding melt pools. In figure (b), the laser displacements (+3), (0), and (-3) denote different focal positions (McLouth et al., 2018).

Changing the focal height away from the focal plane reduces the power density. Exploiting the laser beam's divergence to lower power density presents a novel way of manipulating part microstructure. Compared with other processing parameters, the simultaneous alteration of spot size and power density produces a more pronounced effect on melt pool morphology. As demonstrated in Figure 2-36, the (0) focus shift sample displays a narrower and deeper molten pool morphology than the wider, shallower morphologies evident in the (+3) and (-3) focus shift samples. This variation in laser spot size gives rise to distinct microstructural characteristics. A lower power density results in a coarser microstructure with crystallographic texture, whereas a higher power density promotes finer, more equiaxed grains in PBF-LB/M.

2.4.3.4.3 Continuous and Pulsed Laser

Within PBF-LB/M, laser emission may be either continuous wave (CW) or pulsed wave (PW), as depicted in Figure 2-37 (I). A continuous laser delivers a constant stream of energy without interruption, while a pulsed laser produces discrete bursts, each persisting for a short interval. The continuous emission provides a stable heat source, helping to minimise defects such as gas porosity (Biffi et al., 2018). In contrast, pulsed lasers create transient, localised heating with each pulse, resulting in higher cooling rates and peak power densities than those of continuous lasers. Although the intense energy of pulsed lasers can cause severe vaporisation of volatile elements, it also leads to a finer microstructure due to rapid cooling (Ravi et al., 2016). As

shown in Figure 2-37 (II), from a crystallographic perspective, continuous wave lasers are more likely to yield larger, preferentially oriented grains (Karami et al., 2020), whereas pulsed wave lasers tend to promote a more homogeneous and refined microstructure.

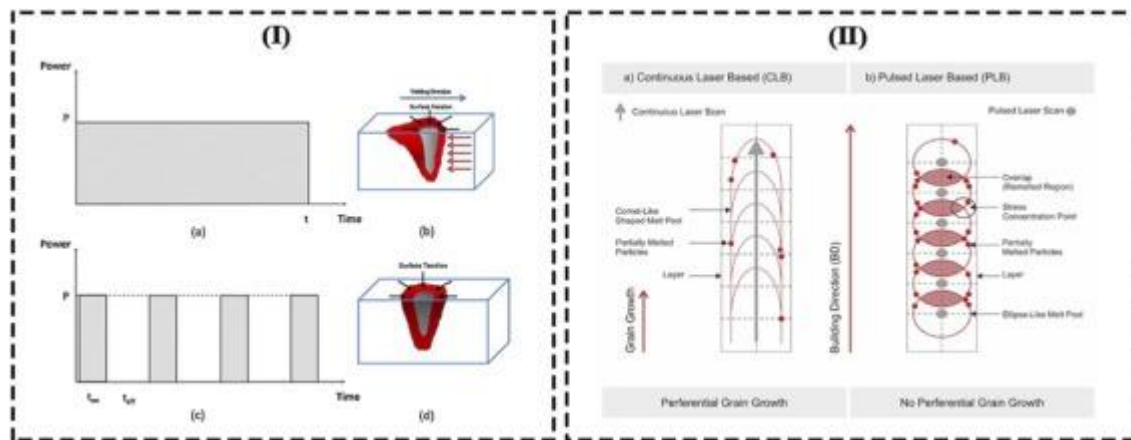


Figure 2-37 (I) Schematic illustration of continuous wave (CW) and pulsed wave (PW) lasers employed in PBF-LB/M processing (Biffi et al., 2018). (II) Melt pool geometries resulting from different laser emission modes (Karami et al., 2020).

Li et al. compared the microstructures produced by continuous and pulsed lasers during PBF-LB/M processing of Inconel 718 (S. Li et al., 2017). They reported that the pulsed laser creates a circular melt pool characterised by periodic, heartbeat-like movements and cooling rates twice as fast as those achieved by the continuous laser. This higher cooling rate resulted in finer columnar dendrites within the microstructure. Similarly, Chou et al. noted the formation of refined epitaxially grown grains in A356 alloy processed with a pulsed laser (Chou et al., 2018). These results underline the ability of pulsed lasers to significantly influence the final microstructure. Specifically, the circular melt pool shape and periodic movements associated with pulsed lasers can produce refined dendritic structures and finely epitaxial grain growth. The choice between continuous and pulsed lasers depends upon the target microstructure and particular application requirements. Continuous lasers are typically favoured when fabricating fully dense, large-scale components, whereas pulsed lasers offer advantages when aiming for finer microstructures and enhanced mechanical properties. The decision regarding laser emission mode should take into account factors such as preferred microstructure, cooling rates, vaporisation phenomena, and the overall demands of the process.

2.4.3.5 Auxiliary Fields

Auxiliary fields have been utilised in PBF-LB/M to control microstructure and defects. Auxiliary fields reported in the literature include magnetic fields, ultrasonic fields, thermal fields, deformation fields, electric fields, and plasma fields. In this section, only the most frequently employed fields—the magnetic field and acoustic field—are reviewed.

2.4.3.5.1 Magnetic Field

The use of a magnetic field (MF) in the PBF-LB/M process has demonstrated potential for enhancing heat dissipation, minimising temperature gradients and residual stress, improving dimensional accuracy, and altering the microstructure, as illustrated in Figure 2-38 (I) (L. Chen et al., 2019). The MF influences the geometry of the melt pool and induces modifications in the microstructure. When a MF is applied during PBF-LB/M, the solidification microstructure can be refined compared to alloys produced by conventional casting methods. It can also modify the texture of the as-built alloys. In particular, the MF can encourage the formation of equiaxed grains and diminish the $\langle 001 \rangle$ texture (for FCC structures) by fragmenting dendrites and promoting the development of new grains. Du et al. investigated the texture evolution of AlSi10Mg during PBF-LB/M with and without ML, as shown in Figure 2-38 (II) (Du et al., 2022). Their results indicated that a 0.2T MF can yield a refined microstructure with a weakened $\langle 001 \rangle$ texture. The finer grain size and reduced anisotropy were attributed to the breakdown of dendrites under high thermoelectric magnetic forces within the melt pool, with the resulting fragments acting as nuclei to suppress the growth of columnar grains and foster the formation of new grains (Du et al., 2022; Z. Zhang et al., 2023). However, the MF was also found to cause grain coarsening and enhance epitaxial growth, as it can restrict the melt flow and counteract reverse flow under its damping effect. This has been confirmed by experimental observations during the DED of Inconel 718 alloy using the auxiliary MF (Du et al., 2020). It has also been reported that the ML can suppress precipitate formation. For example, the application of ML in the wire arc additive manufacturing of Inconel 718 reduced the volume fraction of the Laves phase from 2.4% to 1.3% (Huan et al., 2022). This indicates that the presence of an MF may inhibit the formation of undesirable precipitates in certain alloys, potentially improving their properties.

Furthermore, the MF has been found to decrease both porosity and cracking (Figure 2-38 (II)). For instance, Du et al. observed a significant reduction in the porosity of AlSi10Mg when a 0.12T vertical MF was employed during the PBF-LB/M process (Du et al., 2019). The reduction in porosity was attributed to the mitigation of Marangoni convection and the release of trapped gas from the melt pool. Similar outcomes were reported by Zhou et al., who densified the PBF-LB/M-processed 316 stainless steel using both static and alternating MF (H. Zhou et al., 2022). Seidel et al. applied an MF during DED to minimise the hot cracking observed in the MAR-M-247 nickel superalloy (Seidel et al., 2020). They found that while hot cracking was drastically reduced, liquation cracking still persisted when MF was applied. However, the mechanism behind the reduction in cracking resulting from the application of MF is not yet fully understood.

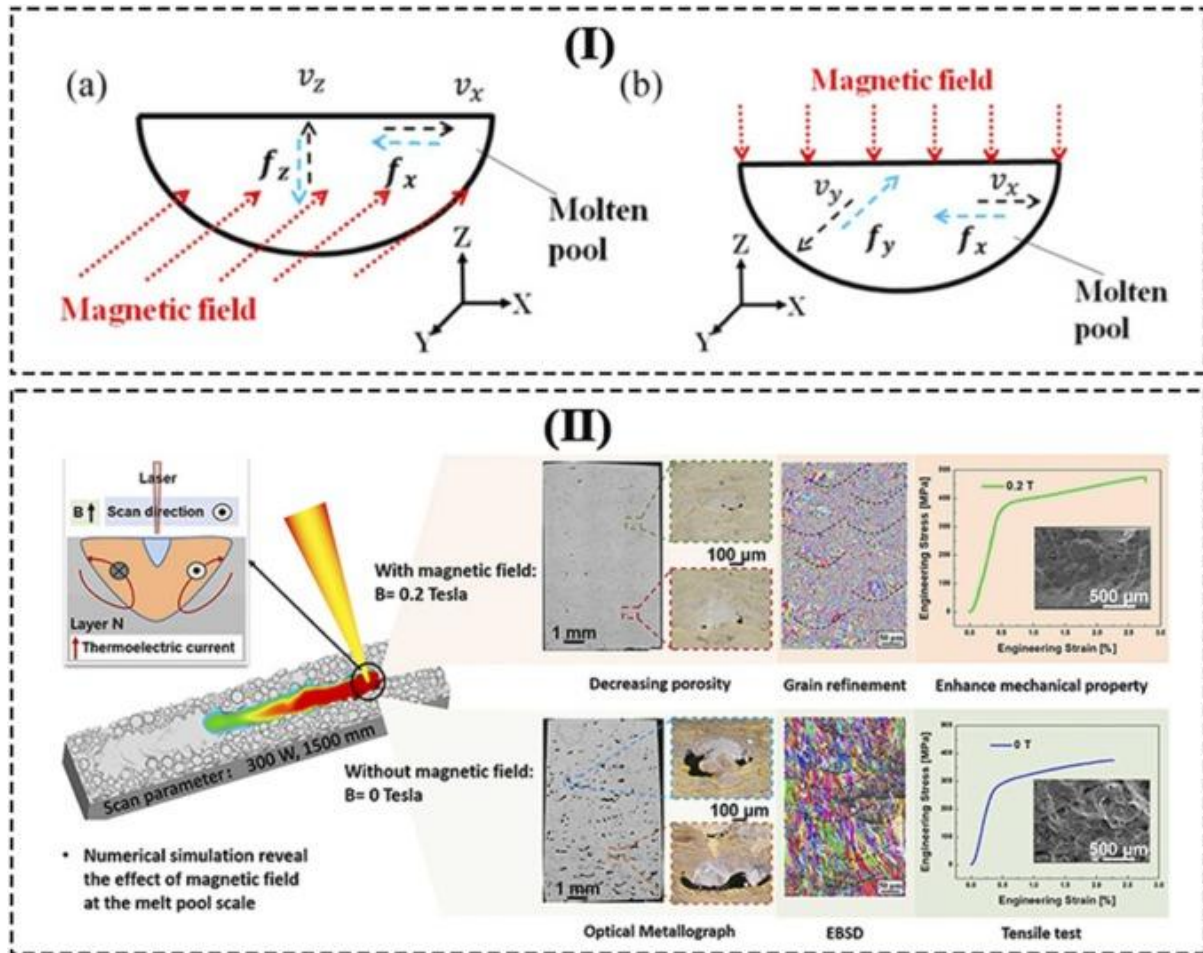


Figure 2-38 Application of a magnetic field (MF) in PBF-LB/M. (I) Lorentz force produced within the melt pool (L. Chen et al., 2019). (II) The external MF diminishes porosity and refines grain structure in PBF-LB/M (Du et al., 2022).

2.4.3.5.2 Acoustic Field

Owing to the steep temperature gradient during the PBF-LB/M process, the $\langle 001 \rangle$ //BD texture is preferentially formed. The ultrasonic generator produces a high-frequency oscillating voltage, which results in vertical ultrasonic vibrations on the surface of the substrate. The output power and amplitude of the ultrasonic wave can be adjusted via a knob. However, excessively intense ultrasonic vibrations may cause powders to accumulate at the ultrasonic node, thereby compromising the flatness of the powder bed and the subsequent printing process. There are marked differences in the morphology and shape of the molten pool when prepared with, as opposed to without, ultrasonic assistance. In particular, the molten pool depth is considerably increased when ultrasonic assistance is applied (Todaro et al., 2020). Ultrasonic fields induce acoustic streaming, cavitation and vibration through mechanical waves, which can exert various effects on the PBF-LB/M process, as illustrated in Figure 2-39 (Z. Yan et al., 2023). Furthermore, during the process of ultrasonic-assisted PBF-LB/M, the fracturing of dendrite tips creates numerous sites for heterogeneous nucleation, leading to the CET transformation and the elimination of the directional texture (C. Tan et al., 2023).

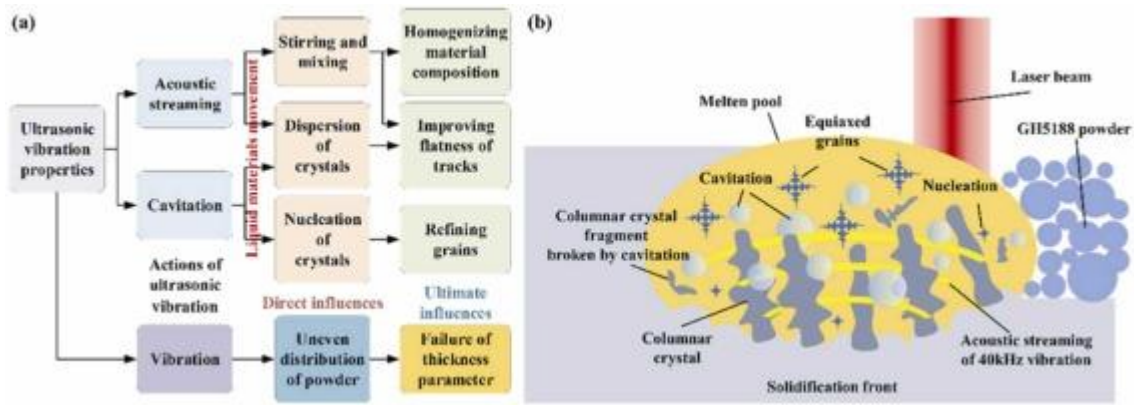


Figure 2-39 (a) The influence of ultrasonic vibration in ultrasonic-assisted PBF-LB/M, and (b) the melt pool generated during PBF-LB/M assisted by ultrasonic vibration (Z. Yan et al., 2023).

The interaction mechanism between the acoustic field and materials is primarily governed by acoustic streaming and cavitation (Ji et al., 2022). The use of an ultrasonic field in PBF-LB/M has been investigated to alter the microstructure, surface finish, and mechanical properties (C. Shi et al., 2018). Acoustic streaming enhances compositional uniformity by stirring and mixing molten metals, which is essential during the solidification process (Ji et al., 2022). It equalises the temperature distribution within the melt pool, thereby reducing significant temperature gradients and preventing preferential grain growth, resulting in a more consistent microstructure (Tilita et al., 2020). Todaro et al. demonstrated that the presence of an ultrasonic field promoted CET transformation, leading to randomly oriented equiaxed grains and grain refinement during ultrasonic-assisted additive manufacturing of 316 L stainless steel (Todaro et al., 2021). Owing to the acoustic streaming and stirring effect induced by the acoustic field, the fluidity of the melt pool is increased. The vibrations produced by the ultrasonic field can disrupt gas bubbles trapped within the molten pool, thereby facilitating gas escape and reducing porosity (Todaro et al., 2021). Ning et al. reported that during ultrasonic-assisted laser additive manufacturing of Fe-Cr stainless steel, porosity, micro-cracks, and grain size were significantly reduced as a result of ultrasonic vibration (Ning & Cong, 2016).

Cavitation is the primary mechanism responsible for microstructure refinement (Todaro et al., 2020). Ultrasound can induce cavitation in the melt pool, breaking up dendrites and acting as a catalyst for heterogeneous nucleation during the crystallisation process (Balasubramani et al., 2023). For instance, Wang et al. examined the fragmentation and refinement of primary amorphous particles in an Al-35Cu alloy induced by ultrasonic melt treatment, further evidencing the microstructural refinement capabilities of ultrasound (F. Wang et al., 2017). However, the effects of the ultrasonic field in PBF-LB/M depend on parameters such as frequency, amplitude, duration, and the properties of the material being processed. For example, high ultrasonic frequency might lead to porosity (H. Wang et al., 2020). Further research and optimisation are necessary to fully understand and exploit the potential benefits of incorporating ultrasonic energy into the PBF-LB/M process.

In summary, several field-assisted approaches, including magnetic and ultrasonic fields, have been explored and applied to the PBF-LB/M process to tailor the microstructure and reduce defects. These techniques have the potential to enhance the quality and properties of manufactured components by controlling solidification behaviour, reducing porosity, refining grains, and modifying texture. However, the applicability of these field-assisted methods may vary depending on the specific materials and process parameters used. Further research and development are needed to fully comprehend and optimise these techniques for PBF-LB/M applications.

2.5 Additively Manufactured Ti6Al4V Alloy

Ti6Al4V components are traditionally manufactured using methods such as forging, cold and/or hot forming, hydroforming, and various machining operations like drilling, milling, and turning, as well as advanced techniques like laser and waterjet cutting. The difficulty in machining titanium and its alloys stems from their low ductility and high tensile strength. The low elastic modulus of alloy can also cause significant “springback” after forming, requiring rigid setups increasing pressure and temperature at tool contact points. At elevated temperatures, chemical reactivity of titanium increases, leading to nitrogen and oxygen absorption at the surface, which may result in microcracks that impair durability and fatigue resistance. Consequently, machining of titanium alloys typically occurs at lower speeds compared to aluminium alloys or steels, extending production times and increasing costs. Additionally, the cost of titanium alloys is notably higher, with a titanium ingot priced around 90 times more than a steel ingot. When combined with high buy-to-fly ratios in traditional machining, which can be as high as 40:1, the overall cost of manufacturing titanium components becomes significantly elevated.

The limitations of conventional manufacturing methods for Ti-based materials underscore the advantages of AM. AM can produce near-net-shape parts with equal or superior quality and significant cost savings (Y. Sun, 2016). The intricate thermal behaviours and high-temperature gradients typical of various AM processes, along with the variable crystal structures of titanium and its alloys, facilitate significant modifications in their microstructure and mechanical properties. Much research in PBF-LB/M has focused on Ti6Al4V due to its excellent strength-to-weight ratio, fracture toughness, corrosion resistance, and biocompatibility (Cui et al., 2011). This alloy is particularly well-suited for laser processing, unlike aluminium alloys, challenging to process due to high reflectivity and susceptibility to cracking (Aboulkhair et al., 2014). Ti6Al4V is widely used in aerospace for components like jet engines and airframes (P. Singh et al., 2017), and in biomedicine for bone implants due to its biological tissue compatibility (Y. L. Hao et al., 2016). There is also growing interest in its application in marine environments due to its corrosion resistance (Oryshchenko et al., 2015). The experimental section of this thesis focuses on microstructural development specific to PBF-LB/M. Selecting Ti6Al4V, a well-researched and robust material for PBF-LB/M, ensures that any observed microstructural changes are due to methodological alterations rather than material-related issues.

2.5.1 Prior β Grain Morphology

PBF-LB/M involves a unique thermal history characterized by directional melting and solidification against the direction of heat transfer. This process is compounded by repeated melting and solidification cycles due to successive laser scans and layer depositions, alongside cyclic heating and cooling post-solidification (DebRoy et al., 2018; L. Qian et al., 2005; Thijs et al., 2010). Figure 2-40 shows a simulated thermal history for a specific point within a PBF-LB/M Ti6Al4V component (Pantawane et al., 2020), illustrating the thermal cycles prompted by different laser scan vectors within a single layer and across multiple layers. After initial solidification in layer P1, the material undergoes several thermal cycles with each new laser scan and layer addition, occasionally leading to the partial re-melting and re-solidification of the material. The combination of high laser power, fast scanning speeds, and a small laser spot size produces exceptionally rapid heating and cooling rates (Bertoli et al., 2017; Y. Li et al., n.d.; J. Wang, Liu, Qin, et al., n.d.; J. Wang, Liu, Rabadia, et al., n.d.). In-situ synchrotron experiments on PBF-LB/M Ti6Al4V have documented maximum heating and cooling rates of approximately 10^6 °C/s and 10^5 °C/s, respectively (Hocine et al., n.d.).

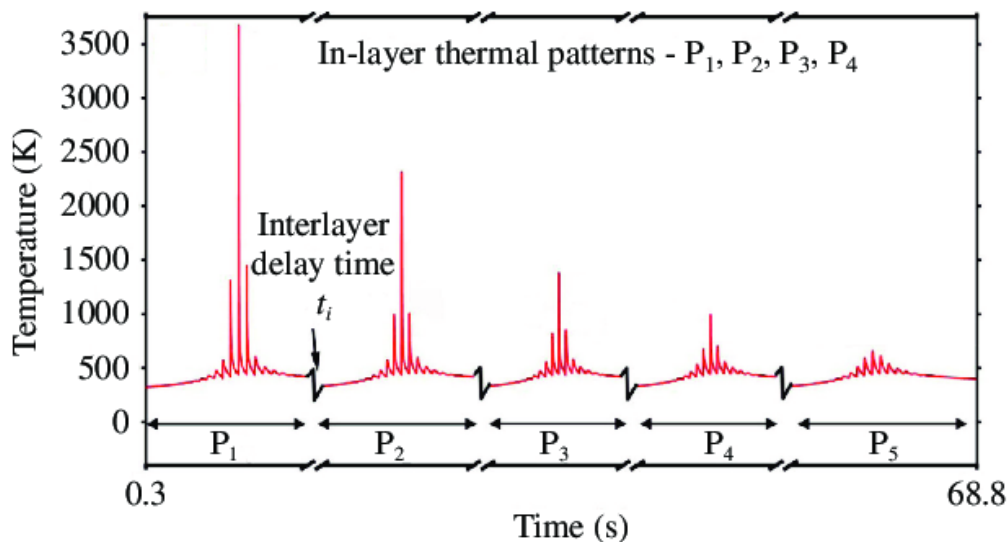


Figure 2-40 Simulated temperature profile at a specific point within PBF-LB/M Ti6Al4V, illustrating re-heating and cooling cycles occurring both within and between layers. The points P1 through P5 denote sequential layers (Pantawane et al., 2020).

The process of directional solidification, combined with rapid cooling and subsequent thermal cycles, leads to a non-equilibrium, hierarchical as-built microstructure characterized by epitaxially grown prior- β grains orienting contrary to the cooling direction. Within these columnar β grains, there exist multiple sets of finely structured acicular α' martensite variants (S. Cao et al., 2017; L. Murr et al., n.d.; Sallica-Leva et al., n.d.; Simonelli et al., 2014; Thijs et al., n.d.; Vilaro et al., 2011; X. Wu et al., n.d.; W. Xu et al., n.d.). The specific processing conditions significantly influence the characteristics of the as-built microstructure. Recent research indicates that increased laser energy density results in broader prior- β grains and finer α' martensite structures (J. Han et al., 2017). Additionally, the partial re-melting of already solidified layers enhances the β solidification texture. As depicted in Figure 2-41, a dominant $\{100\}_\beta$ texture aligned with the growth orientation is evident from the reconstructed β -titanium

phase orientation map (Figure 2-41 (a)), reconstructed using EBSD data of α and/or α' -titanium phase based on the Burgers orientation relationship (Simonelli et al., 2014). It is noteworthy that the direction in which prior- β grains grow depends on the heat flow within the material, which itself is influenced by both the scanning speed and strategy employed (Simonelli et al., 2014; Thijs et al., n.d.). Consequently, the growth trajectory of the prior- β grains may align either parallel or at a specific angle to the overall build direction (Z-axis) (S. Cao et al., 2017; Simonelli et al., 2014). An example of this is shown in the pole figure in Figure 2-41 (c), where the $\{100\}_\beta$ texture direction deviates by about 20° from the macroscopic build direction (Simonelli et al., 2014).

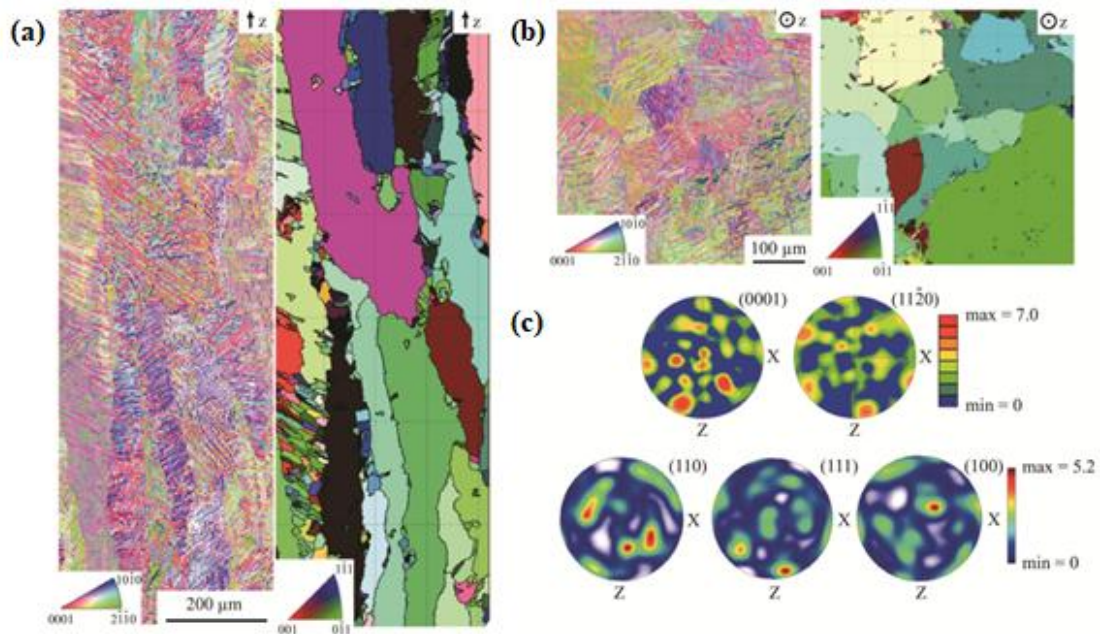


Figure 2-41 Grain orientations and textures in PBF-LB/M Ti6Al4V: (a) orientation mapping of α' and reconstructed β phases on a vertical cross-section (Simonelli et al., 2014); (b) similar mapping on a horizontal cross-section (Simonelli et al., 2014); (c) pole figures of α' and reconstructed β phases derived from the vertical section shown in (a) (Cepeda-Jiménez et al., 2020).

Figure 2-42 (a) shows the alignment of several prior- β grains along the build direction, captured via LOM. Figure 2-42(b) and (c) present an inverse pole figure (IPF) map and its corresponding reconstructed prior- β grain. The subsequent figures, Figure 2-42(c) to (f), illustrate the influence of wall thickness changes on β grain structure (A. Antonysamy, 2012). A shift from 1mm to 5mm in thickness significantly alters the prior- β grain structure. At wall thicknesses less than 2 mm, the grains display a curved exterior morphology, resulting from the grains initiating growth from the periphery of the powder bed inward, following the melt pool contour until they intersect with upward-growing β grains from a lower layer where powder-based nucleation was not possible (A. Antonysamy, 2012). This curved grain formation is influenced by factors such as small melt pools, directional heat transfer, and rapid cooling, promoting columnar grain growth. Observations of columnar grains in AMed Ti6Al4V across various AM methods have been widely reported (Baufeld et al., 2009; Lancaster et al., n.d.; Mandil et al., 2016; Sandgren et al., n.d.; Simonelli et al., 2014; Vrancken et al., 2012; F. Wang et al., 2013). Figure 2-43(a) explains the mechanism for columnar β grain formation in AM, where dendritic

growth starts from existing β grains within the solid β interface extending into the liquid+ β phase. The solidification range for Ti6Al4V liquid+ β , ΔT_{fr} , is around 5K (M. Bermingham et al., 2015), promoting rapid solidification and epitaxial nucleation of β grains. The rapid cooling rates in AM, along with a lack of effective nucleating agents ahead of the β grains, prevent any disruptive nucleation, influencing the dimensions of prior β grains based on the time the material spends above $T_{transus}^{\alpha/\beta}$ temperature.

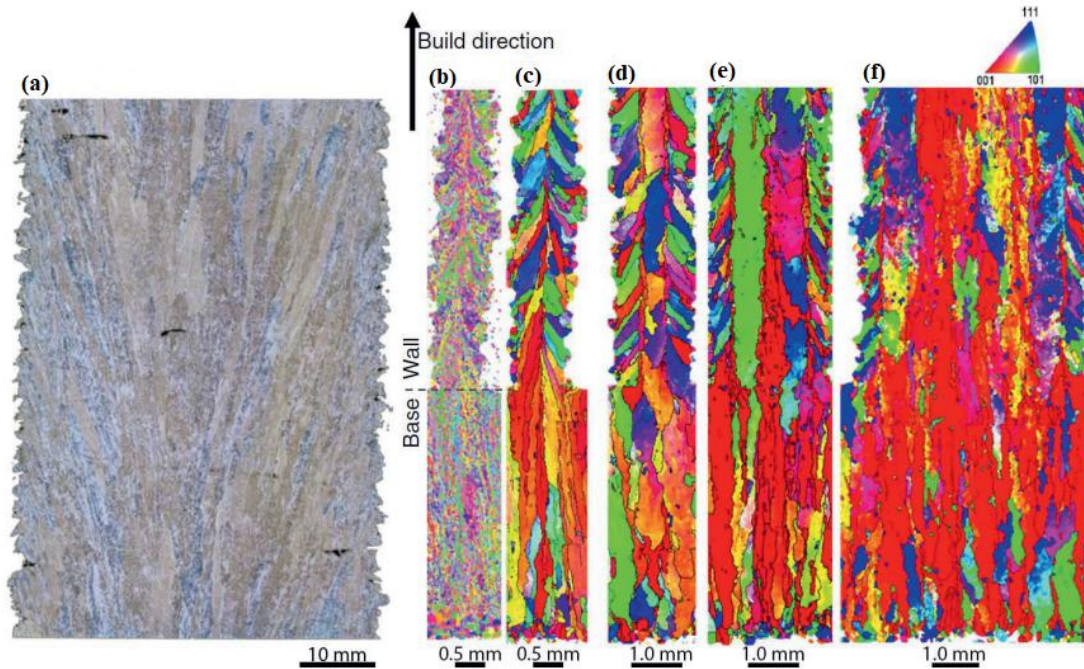


Figure 2-42 A macroscopic view of (a) PBF-EB Ti6Al4V, observed perpendicular to the layers, showing columnar prior β grains. (b) an inverse pole figure (IPF) map with (c) the reconstructed β grains of the same region. Figures (c) through (f) illustrate the effect of the build geometry on the size of prior- β grains in PBF-EB Ti6Al4V, noting changes corresponding to different wall thicknesses: (c) 1 mm, (d) 1.5 mm, (e) 2.0 mm, and (f) 5.0 mm (A. Antonyasamy, 2012).

The size of β grains in Ti6Al4V is not tied to the cooling rate from the transus temperature to room temperature, unlike other microstructural features such as α -laths and colonies. The importance of prior β grains stems from their role in determining the maximum size of α colonies, which cannot grow beyond the β grains from which they originate (Lütjering & Williams, 2003). Various methods can alter the typical columnar structure of β grains. Mechanical deformation, such as rolling applied immediately after wire deposition in WAAM, can transform columnar β grains into an equiaxed structure due to recrystallization within the deformed layer, which is reheated by the deposition of subsequent layers (Martina et al., 2015). Furthermore, incorporating small amounts of boron (up to 0.13 wt.%) into Ti6Al4V has been shown by Bermingham et al. (M. Bermingham et al., 2015) to produce smaller prior- β grains in DED processes, as boron limits the lateral growth of dendrites, allowing more grains to form within a broader solidification range (M. Bermingham et al., 2015). This addition increases the solidification range to about 130K (M. Bermingham et al., 2015), significantly wider than in alloys without boron, promoting lateral precipitation of TiB particles from dendrites, limiting lateral β grain growth and encouraging nucleation of adjacent dendrites. This broader range

also allows slower dendritic solidification, leading to more irregular grain shapes and a varied heat dissipation pattern, as illustrated in Figure 2-43 (b).

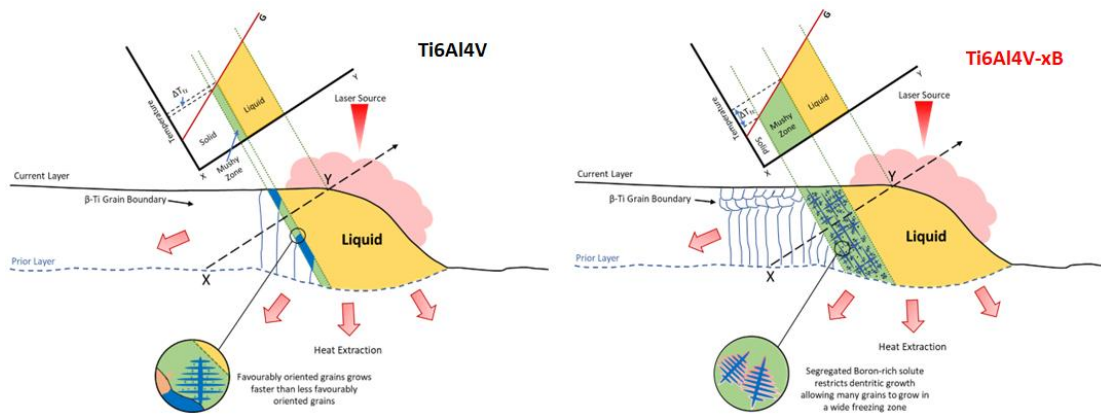


Figure 2-43 β grain growth in DEDed Ti6Al4V, showing (a) without boron and (b) with boron addition. The inclusion of boron extends the solidification range ΔT_{fr} , or the liquid+solid zone, from 5K to 130K adapted from (M. Bermingham et al., 2015).

Research has shown that small amounts of the β phase are present in samples made with high laser power or narrow hatch distances, as identified through synchrotron XRD (Voisin et al., 2018), EBSD (D. Zhang et al., n.d.), and TEM (Barriobero-Vila et al., 2017) analyses. Figure 2-44 (a) illustrates the $\alpha+\beta$ microstructure located in the core of a specimen produced using a narrow hatch distance (Barriobero-Vila et al., 2017). Both the utilization of high laser power and the application of a narrow hatch distance contribute to elevated in-situ temperatures and prolonged periods of high temperatures during the inherent thermal cycles of the process (Hocine et al., 2020), promoting the transition of metastable martensite into $\alpha+\beta$ phases. Beyond the β phase, some research has also unveiled α_2 precipitates within the as-built samples, as determined through TEM and synchrotron XRD investigations (Barriobero-Vila et al., 2017; Thijs et al., 2010). Figure 2-44 (b) displays the superlattice reflections indicative of α_2 precipitates within α lamellae, likely caused by thermal cycling near the α_2 solvus point. Adjusting the aluminium and oxygen content of Ti6Al4V powders, along with maintaining a low oxygen environment during printing, may help in minimizing α_2 precipitation.

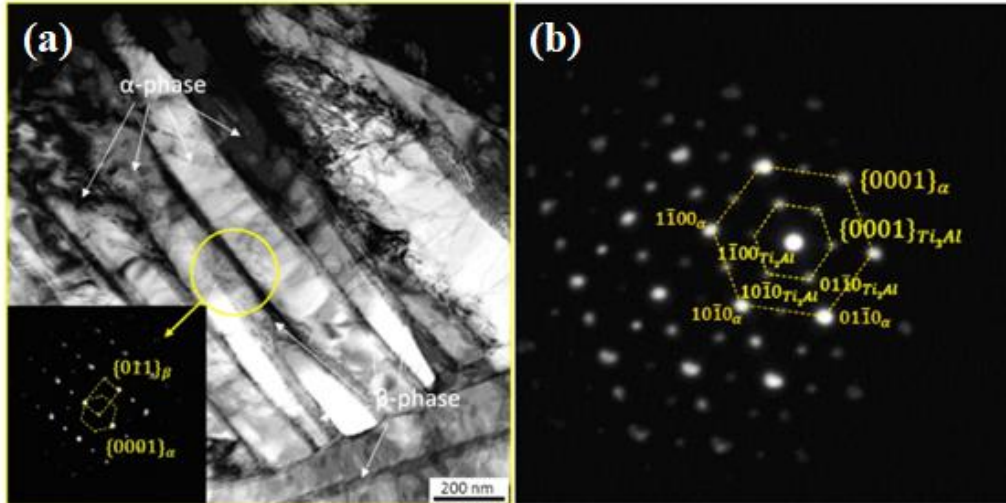


Figure 2-44 Detection of β and α_2 phases in PBF-LB/M Ti6Al4V: (a) TEM (BF) image displaying the $\alpha+\beta$ microstructure at mid-height ($Z\sim 5$ mm) of a specimen; (b) SAD pattern highlighting the structured α_2 phase within an α lamella (Barriobero-Vila et al., 2017).

PBF-LB/M fabricated Ti6Al4V typically shows a predominantly α' martensitic structure. Due to the thermal cycles experienced during fabrication, the α' martensite develops a hierarchical structure varying in width and length, classified into primary α' to quartic α' types. A comprehensive study has recently delved into the intricate details of their development mechanisms (J. Yang, Yu, et al., 2016). Within α' martensite phase, various lattice defects such as dislocations, stacking faults, and twins are common (Fotovvati et al., 2012; Haubrich et al., n.d.). A significant concentration of dislocations in the α' plates has been observed via TEM (Voisin et al., 2018) and evidenced from the broadening of diffraction peaks in high-energy XRD studies (D. Zhang et al., n.d.). Dislocation analysis via TEM identified both $\langle a \rangle$ and $\langle c+a \rangle$ type dislocation within the α' martensite, suggesting significant plastic deformation occurs during PBF-LB/M fabrication process (Voisin et al., 2018). Theoretically, for α -titanium, specific twins are likely to form under compression along the c-axis, namely $\{10\bar{1}1\}\langle 10\bar{1}2 \rangle$ and $\{11\bar{2}2\}\langle 11\bar{2}3 \rangle$ twins, while tension along the same axis can lead to the formation of $\{10\bar{1}2\}\langle 10\bar{1}1 \rangle$ and $\{11\bar{2}1\}\langle 11\bar{2}6 \rangle$ twins (Kumar et al., n.d.). In PBF-LB/M fabricated Ti6Al4V, studies have identified both compression $\{10\bar{1}1\}$ (S. Cao, Chu, et al., n.d.; Z. Xie et al., n.d.) and $\{11\bar{2}2\}$ twins (Voisin et al., 2018), as well as tension $\{10\bar{1}2\}$ twins (Kazantseva et al., n.d.; Krakhmalev et al., n.d.; Voisin et al., n.d.; J. Yang, Yu, et al., n.d.), as depicted in Figure 2-45. Previous research has suggested that tension $\{10\bar{1}2\}$ twins might help accommodate tensile residual stress in the upper regions of PBF-LB/M parts (Krakhmalev et al., n.d.), yet this theory does not fully account for the simultaneous presence of both compression and tension twins in a single TEM sample. Certain studies link twinning to the martensitic transformation from $\beta \rightarrow \alpha'$ (S. Cao, Chu, et al., n.d.; Matsumoto et al., n.d.), though this mainly explains the activation of $\{10\bar{1}1\}$ twins. A more recent analysis proposed that the combined effects of rapid thermal cycling to peak temperatures and the resultant solid-state phase transformations could be responsible for the simultaneous formation of both compression and tension twins in PBF-LB/M Ti6Al4V (S. Cao, Zhang, et al., n.d.).

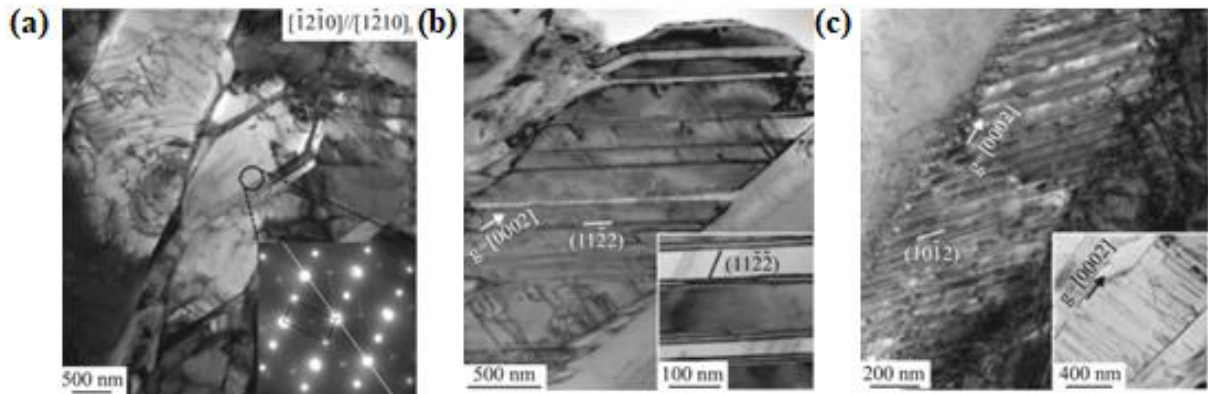


Figure 2-45 Lattice Defects in PBF-LB/M Ti6Al4V: (a) Type $\{10\bar{1}1\}<10\bar{1}2>$ twin [211]; (b) Type $\{11\bar{2}2\}<11\bar{2}3>$ twin (Voisin et al., 2018); (c) Type $\{10\bar{1}2\}<10\bar{1}1>$ twin (Voisin et al., 2018).

Alongside hexagonal α' martensite, the presence of orthorhombic α'' martensite in as-built Ti6Al4V has been noted in several studies (Kazantseva et al., 2018; L. Murr et al., n.d.; Z. Xie et al., n.d.). Specifically, α'' martensite was identified in one of the Ti6Al4V samples, particularly in a cuboid with a longer horizontal (XY) cross-section. This phenomenon was attributed to the increased cooling effect due to a greater area for heat dissipation on the horizontal plane, which could potentially trigger the formation of α'' martensite (Z. Xie et al., n.d.). Within the PBF-LB/M process, thermal cycles may raise the temperature of previously consolidated layers to intermediate levels within the $\alpha+\beta$ phase region. At such temperatures, the segregation of elements can enrich the β phase with vanadium. Consequently, cooling rapidly from these intermediate temperatures is likely to cause the development of α'' martensite (Kazantseva et al., 2018).

PBF-LB/M Ti6Al4V, when compared to thermo-mechanically treated counterpart, demonstrates superior strength but reduced ductility. This difference arises from the non-equilibrium fine lamellar α' martensitic (Sallica-Leva et al., n.d.; W. Xu et al., n.d.; J. Yang, Han, et al., n.d.; J. Yang, Yu, et al., n.d.) and the accumulation of residual stress throughout the PBF-LB/M fabrication (Facchini et al., 2010; Vrancken et al., 2012). Consequently, both in-process adjustments and post-process treatments are being investigated to promote the transformation of metastable martensite into stable $\alpha+\beta$ phases to produce a ductile microstructure, as well as decrease anisotropy and residual stress.

2.5.2 Mechanical Properties

The PBF-LB/M process creates unique microstructures and defects like porosity and residual stress in Ti6Al4V, affecting its mechanical properties differently compared to wrought materials. The presence of α' martensite generally enhances strength but decreases ductility (S. Cao, Chu et al., 2018). The anisotropic grain structure of as-built material leads to varying performance under different loading directions (Simonelli et al., 2014). Pores, acting as stress concentration points, often trigger early crack formation compared to wrought material (Y. Hu, Wu, et al., 2020). Additionally, the residual stress from rapid cooling can promote crack growth, effectively preloading the material in tension (Leuders et al., 2013).

Tensile and fatigue testing are the common methods for evaluating the mechanical properties of PBF-LB/M Ti6Al4V at ambient temperature. Fatigue testing is vital for components used in dynamic settings like aerospace or biomedical implants, where understanding service life under cyclic stress is crucial. Tensile testing offers a straightforward way to assess mechanical characteristics of PBF-LB/M Ti6Al4V, providing essential comparisons with wrought materials and other research varying in process settings, machine, and heat treatments. A compilation of tensile properties from more than 20 studies, illustrated in Figure 2-46 via a violin plot, reveals median ultimate tensile strength, yield strength, and elongation at 1165 MPa ranging from to 1421 MPa, 1016 MPa ranging from 664 to 1273 MPa, and 7% ranging from 1.6 to 12.7%, respectively. The broad variability in data mainly stems from differences in processing conditions, but the violin plot effectively shows the distribution of reported values. Variations in equipment, lasers, and processing parameters can lead to diverse microstructures and porosity levels, affecting mechanical properties.

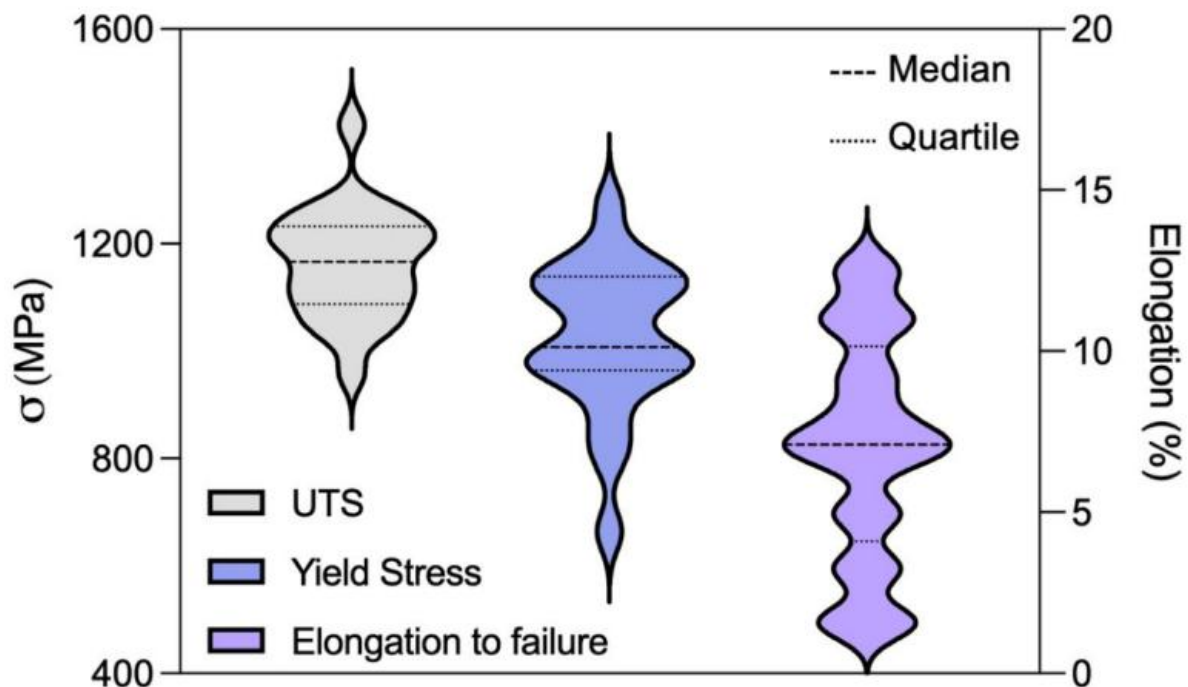


Figure 2-46 A violin plot displaying the spread of 21 data sets on ultimate tensile strength, yield stress, and elongation at failure for PBF-LB/M Ti6Al4V (Edwards et al., n.d.; Facchini et al., 2010; Hollander et al., n.d.; Y. Hu, Wu, et al., n.d.; Kasperovich et al., n.d.; Koike et al., n.d.; Leuders et al., n.d.; S. Liu et al., n.d.; Rafi et al., 2013; X. Shi et al., n.d.; Simonelli et al., n.d.; Vilaro et al., 2011a; Vrancken et al., 2012; Wysocki et al., n.d.; Xing et al., n.d.; R. Zhao et al., n.d.).

Compared to traditionally wrought Ti6Al4V (Leyens & Peters, 2006), analysis of datasets from literature on PBF-LB/M Ti6Al4V shown in Figure 2-46 reveals median UTS and yield strength increase of 22% and 14%, respectively, attributed primarily to the fine acicular α' martensitic structure. Nonetheless, this fine α' phase, along with potential inclusions of oxygen contamination, reduce elongation at failure by 50%, adversely affecting ductility. Given Ti6Al4V is highly sensitivity to oxygen, and the PBF-LB/M process often involving oxygen levels >10 ppm, this can lead to increased oxygen content and consequent brittleness in the

material (X. Li et al., 2005). Heat treatments aim to enhance ductility, often involving stress relief performed below 800°C, which slightly improves elongation by about 1% but slightly reduces strength due to minimal grain growth (X. Yan et al., n.d.). Annealing above 800°C significantly improves ductility by coarsening grains, though it further reduces strength. For instance, Xingchen et al. managed to increase elongation from 6% to 18% with a 900°C treatment, but UTS dropped from 1241 MPa to 945 MPa (X. Yan et al., n.d.). Temperatures just below the transition point lower both strength and elongation, while exceeding this temperature results in poor elongation (4%) and a strength reduction of over 20% compared to PBF-LB/M Ti6Al4V.

Fracture in PBF-LB/M Ti6Al4V often occur along both prior β and α grain boundaries, showing a ductile dimpled texture on the fracture surface (Yadroitsev et al., 2018). The orientation of columnar β grains affects crack propagation, favouring intergranular rather than transgranular propagation. This results in varying mechanical properties and crack growth rates depending on build orientation. Simonelli et al. observed that loading parallel to the grain orientation enhances ductility compared to perpendicular loading (Simonelli et al., 2014), yet both orientations have similar elastic moduli due to a weak α' texture minimally affecting the modulus. Despite increased ductility when loaded in the build direction, Cain et al. reported that residual stresses, significantly in the build direction and reaching to 200 MPa, can accelerate crack growth by contributing to the external load (Cain et al., 2015).

Fatigue properties of PBF-LB/M Ti6Al4V components draw significant interest from industries like aerospace, automotive, and biomedical due to the demand for dynamic parts with extended service lives. The presence of stress concentrators such as surface imperfections, internal pores, and residual stresses typically results in PBF-LB/M Ti6Al4V having a notably reduced fatigue life compared to wrought counterparts (Pessard et al., 2021). Fatigue testing parameters vary widely, contributing to challenges in comparing data across different PBF-LB/M Ti6Al4V studies. These variables include loading direction (uniaxial, bending, torsional), testing temperatures (including elevated temperatures for simulating operational environments), stress cycles (with most studies opting for a constant amplitude stress waveform and varying stress ratios), as well as the frequency of applied stress, typically ranging from 10 to 100 Hz based on the type of loading. Data gathered from various studies performing room temperature, uniaxial fatigue tests with a stress ratio of $R=0.1$ has been visualized in Figure 2-47 as a violin plot to examine the distribution and range of fatigue limit under as-built and HIPed conditions. HIPing, aimed at defect repair to enhance fatigue performance, and data from surfaces refined by machining were specifically considered, as surface defects notably reduce fatigue life. The median fatigue limit for as-built and machined specimens was identified at 425 MPa (with a range of 340 – 550 MPa), while for HIPed and machined specimens, it was at 570 MPa (with a range of 430 – 690 MPa). In PBF-LB/M components free from surface flaws, fatigue fractures usually originate from pores or microstructural inhomogeneities and are further intensified by residual stresses (P. Li et al., n.d.).

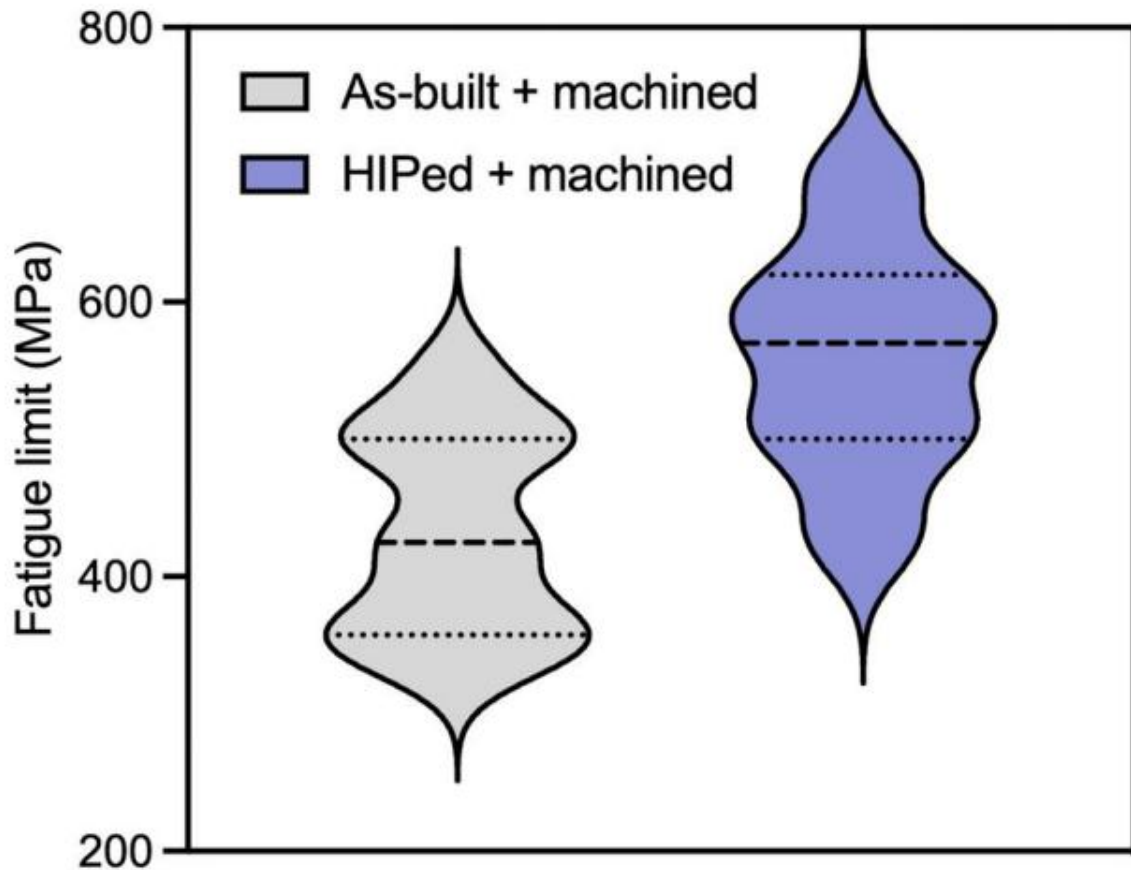


Figure 2-47 A violin plot illustrating the distribution of high cycle fatigue limits for machined LPBF specimens under a stress ratio of $R = 0.1$, comparing as-built and HIPed conditions, based on 17 studies (Bagehorn et al., n.d.; Gong et al., n.d.; Y. Hu, Wu, et al., n.d.; Kahlin et al., n.d.; Kasperovich et al., n.d.; Leuders et al., n.d.; Masuo et al., n.d.; Rafi et al., 2013; Wycisk et al., n.d., 2013; K. Zhang et al., 2010; X. Zhao et al., n.d.).

Internal pores and surface roughness notably deteriorate fatigue life of PBF-LB/M component by serving as stress concentrators. In nearly fully dense parts (99.9%), surface irregularities can impact fatigue life more severely than pores (Chastand et al., 2018), as rough surfaces create multiple stress concentrators akin to small cracks (Suraratchai et al., 2008), while pores act as singular stress concentrators. Surface roughness can be mitigated through methods like machining or polishing, yet some internal porosity typically remains, affecting mechanical properties. Various studies have explored pore size effects on fatigue life by deliberately incorporating defects into components (Wilson-Heid et al., 2021.), though these engineered pores might react differently compared to naturally occurring melt pool-related pores. The literature and industry lack specific guidelines for assessing pore characteristics such as size, shape, and distribution on mechanical properties. Despite the absence of specific thresholds, certain pore behaviours have been documented, like Murakami's finding that a cross-sectional area of a defect, perpendicular to the load direction, influences mechanical performance more than pore volume (Murakami, 2016). Failure typically originates from the largest pore if all have similar shapes, but lack of fusion defects with large aspect ratios and sharp edges can be particularly detrimental by acting as crack initiation points.

2.6 Additively Manufactured Ti6Al4V-xB Alloys

2.6.1 Boron Induced Solidification Pathways in AM

Boron can be incorporated in its elemental form into a material by either blending it into the powder in its pre-alloyed state or by mixing it directly with the feedstock powder. When mixing boron directly, it is crucial to ensure even distribution throughout the mixture. Methods such as ball milling are often employed to achieve this without altering the natural shape and size distribution of titanium or its alloys particles (Attar et al., n.d.; Y. Hu et al., 2017). Moreover, maintaining the feedstock “flowability” is a key consideration. Certain additive manufacturing (AM) techniques might necessitate unique approaches. For instance, WAAM might require coating the substrate with a boron-containing paint (M. Bermingham, Kent, et al., 2015).

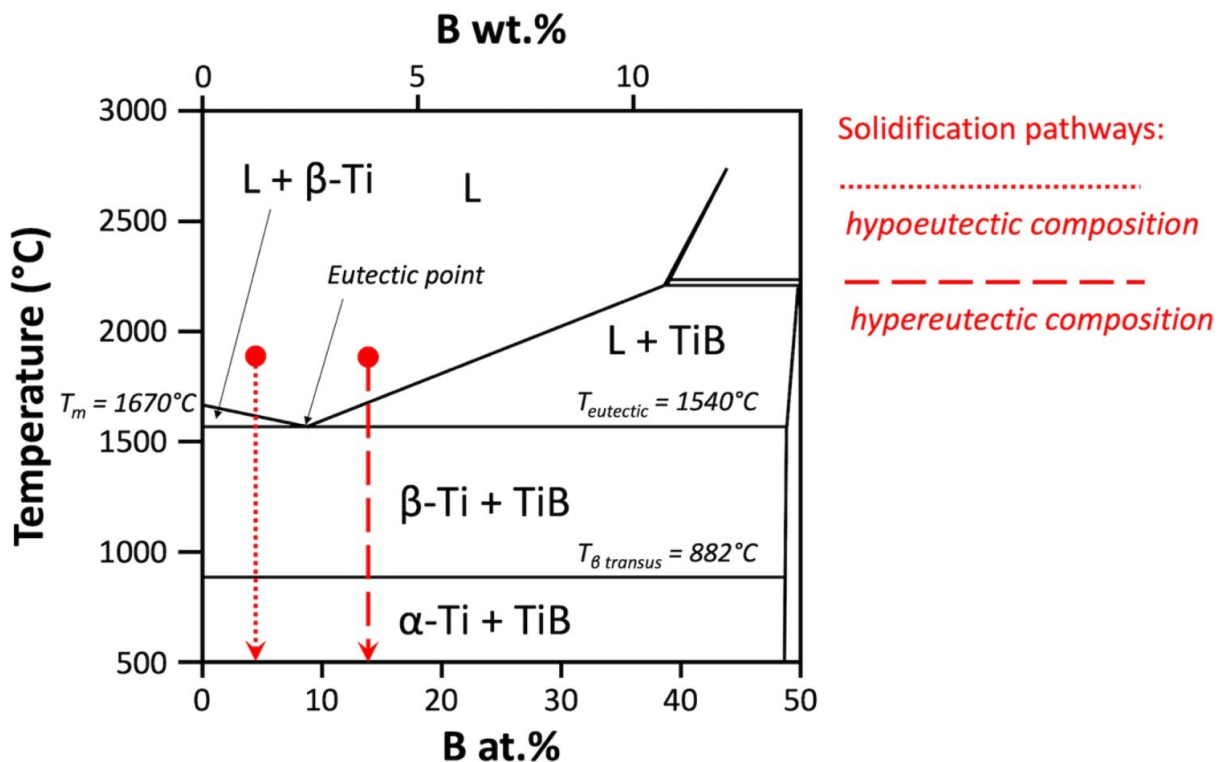


Figure 2-48 Binary phase diagram of Titanium-Boron showing concentrations of up to 50 at%B.

Boron dissolves completely in liquid-Ti phase (Tamirisakandala et al., 2006), but its behaviour upon cooling varies with its concentration. The binary phase diagram, depicted in Figure 2-48, indicates that a eutectic composition exists at Ti-1.6B (wt.%) at 1540°C (R. Banerjee et al., 2004). Concentrations below this eutectic threshold are often regarded as Boron-enhanced titanium alloys, sharing similar characteristics with the base metal/alloy sans boron. Yet, even these hypoeutectic compositions might feature eutectic TiB precipitates, classifying them as discontinuously reinforced metal matrix composites (TMCs) (Shishkovsky et al., n.d.). The classification of materials as hypereutectic or hypoeutectic based on the equilibrium phase diagram becomes less clear in AM, due to the dynamic nature of melt pool. Factors like energy density and Marangoni flow efficiency play a crucial role in even distribution of boron within the melt pool (Das, Balla, et al., n.d.; Galvan et al., 2004). Moreover, the rapid solidification process in AM might limit boron diffusion, leading to B entrapment in super-saturated matrix and potentially altering the eutectic point (Galvan et al., 2004; J. Otte, Zou, et al., n.d.; Pouzet

et al., n.d.). As a result, despite the nominal composition of the starting powders, boron concentration in the melt pool may vary, occasionally reaching hypereutectic levels (Y. Hu et al., 2017; Y. Hu, Ning, et al., n.d.). Figure 2-49 illustrates the solidification paths for both hyper- and hypo-eutectic compositions.

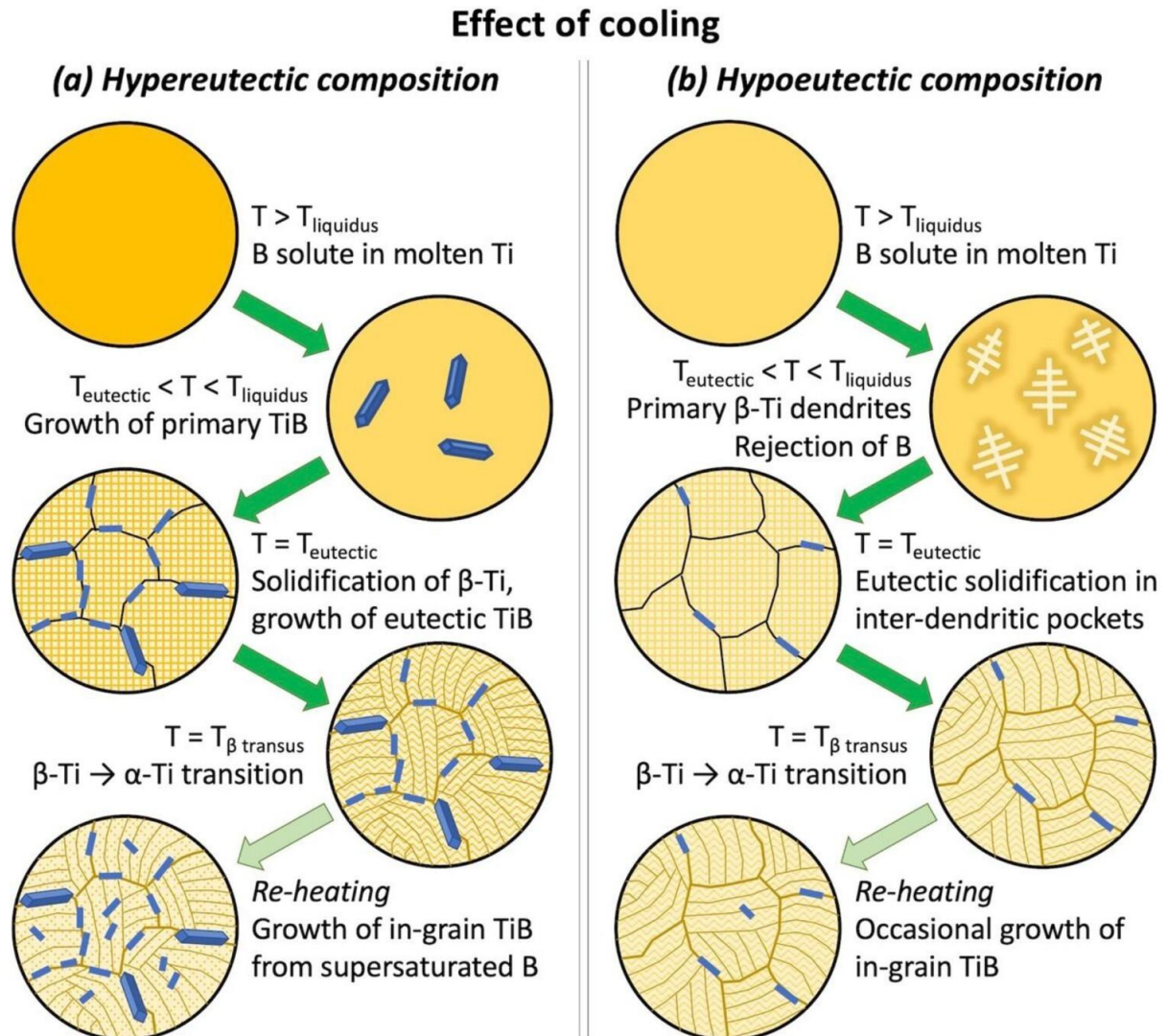


Figure 2-49 Microstructural transformations during cooling for (a) hypereutectic and (b) hypoeutectic alloy compositions.

2.6.1.1 Hypereutectic Compositions

In hypereutectic alloys, indicated by a dashed line in Figure 2-48, the solidification process proceeds as follows: Liquid $\rightarrow$ Liquid + Primary (proeutectic) TiB $\rightarrow$ Primary TiB + Eutectic TiB + β -Ti $\rightarrow$ Primary TiB + Eutectic TiB + α -Ti. This sequence of transformation is depicted in Figure 2-49(a). For titanium alloys, the resulting room temperature phase may be both α and/or β , depending on the alloy specific composition. Though rapid cooling in AM might lead to some deviations from this equilibrium (Galvan et al., 2004), hypereutectic structures typically feature large, prism-shaped pro-eutectic TiB particles alongside a distribution of finer, needle-like eutectic TiB nanowires/whiskers within an α and/or β -Ti matrix (R. Banerjee, Collins, et al., n.d.; R. Banerjee et al., 2004; Chao et al., n.d.; Y. Hu, Ning, et al., n.d.).

Interestingly, these coarse primary TiB precipitates might encapsulate a nanoscale titanium core, highlighted by Banerjee et al. (R. Banerjee, Collins, et al., n.d.) and Kooi et al. (Kooi et al., n.d.), possibly leading to their occasional description as “hollow”, as observed in studies by Lenivtseva et al. (Yi et al., n.d.) and Xue et al. (A. Xue et al., n.d.).

TiB₂ initially forms in the melt pool through the interaction of titanium and boron, particularly near concentrated boron areas, such as around dissolving boron particles. However, due to the abundance of titanium in these regions, TiB₂ tends to further react with the surrounding matrix, resulting in additional TiB (J. Avila et al., n.d.; Bhuiyan et al., n.d.; J. Otte, Zou, et al., n.d.). Although the creation of TiB₂ is energetically favourable, its actual formation rate can be significantly slow. Experiments conducted by Fan et al. (Fan et al., n.d.) on diffusion bonding, involving Ti6Al4V foils and SiC fibres coated with C/TiB_x, demonstrated that the diffusion coefficient of boron in TiB along its needle direction is approximately 45 times greater than in TiB₂, despite both having the same diffusion activation energy of 187-190 kJ/mol.

Hu et al. (Y. Hu, Ning, et al., n.d.; M. Koo et al., n.d.) elucidate during solidification, liquid-titanium solidifies into β -titanium through two pathways: heterogeneous nucleation at primary TiB crystal surfaces and homogeneous nucleation directly from the liquid. Boron, due to its large atomic radius (1.17 Å), exhibits limited diffusivity and solubility in solid titanium. Consequently, boron is expelled into the remaining liquid, where it reacts with liquid-titanium to yield eutectic TiB nanowhiskers (Tamirisakandala et al., 2006). These nanowhiskers tend to cluster at the perimeter of newly formed β -titanium particles (Y. Hu, Ning, et al., n.d.; Tamirisakandala, Bhat, Tiley, et al., n.d.). Similarly, proeutectoid TiB precipitates amass at the β -Ti grain boundaries, potentially acting as sites for subsequent eutectic TiB formation (J. Otte, Zou, et al., n.d.).

The rapid solidification characteristic of AM processes raises concerns about insufficient time for complete eutectic reaction between titanium and boron, possibly leading to boron supersaturation in the solidified β -Ti phase (Rashid et al., n.d.). However, it is important to recognize the diversity in AM techniques, exhibiting various cooling rates. For instance, PBF-EB experiences cooling rates significantly lower than those in PBF-LB/M (C. Li et al., n.d.). Cooling rates in PBF-LB/M can exceed 10⁵ °C/s, are between 10² and 10⁴ °C/s for DED-LB, and hover around 10² °C/s for WAAM (M. Bermingham et al., 2020). Under certain conditions, cooling rates in WAAM can drop further, mirroring those found in casting processes (M. Bermingham et al., 2007; Gudur et al., n.d.). Even if the rapid cooling disrupts eutectic reaction, local re-heating from subsequent layer depositions can promote the separation of the matrix into eutectic TiB and β -Ti (R. Banerjee et al., 2004a). This process leads to the formation of fine TiB particles within the titanium grains due to repeated thermal cycles (R. Banerjee, Genc, et al., n.d.; L. Wang et al., 2023). These later-forming TiB nanowhiskers, growing through solid-state reactions in the supersaturated α matrix, help create well-defined orientation relationships (ORs) and strong TiB-Ti interfaces (R. Banerjee, Genc, et al., n.d.). Despite the formation of additional TiB nanowhiskers within the grains during subsequent reheating phases, the preferential arrangement of primary and eutectic TiB at the β -Ti grain boundaries persists through the $\beta \rightarrow \alpha$ transformation (Y. Hu, Cong, et al., n.d.; Y. Hu, Ning, et al., n.d.; Y.

Hu, Zhao, et al., n.d.). The development of quasi-continuous network (QCN) of TiB reinforcements enhances strength at the grain boundaries while maintaining ductility within the grains, offering a balanced improvement to the overall properties.

As the temperature drops, TiB serves as a potent nucleating agent for heterogeneous nucleation of the α phase. Yang et al. (Y. Yang et al., n.d.) highlight a commonly overlooked phenomenon: at approximately 884-886°C, a peritectoid reaction takes place where β -Ti and TiB react upon cooling to form α -Ti (β -Ti+TiB $\rightarrow\alpha$ -Ti) (Cisar, 1955; Murray et al., 1986). This reaction is commonly disregarded due to its proximity to the α/β transus of pure titanium, which is at 882°C. However, the presence of boron is known to elevate the α/β transus in Ti6Al4V (M. Bermingham, McDonald, Nogita, et al., n.d.; Tamirisakandala, Bhat, Miracle, et al., n.d.). Nonetheless, this peritectoid reaction highlights the significant role of TiB in α phase nucleation, especially when its lattice parameters closely match those of α -Ti and specific crystallographic orientation relationships are present (Y. Yang et al., n.d.).

Yang et al. (Y. Yang et al., n.d.) calculated the lattice mismatches between the “ a ” axis of HCP α -Ti and the “ c ” axis of orthorhombic TiB to be 3.6% and 2.8% along respective “ c ” axes, though these can vary with different chemistry and processing conditions (Y. Yang et al., n.d.). The ORs between TiB and α -Ti are complex due to influenced by the α/β transus. Despite potential deviations in AM from heating and cooling cycles, the $\beta\rightarrow\alpha$ transformation adheres to the Burgers orientation, resulting in 6 variants without or 12 variants including directions in α -phase nucleation (Germain et al., n.d.). Ozerov et al. (Ozerov et al., n.d.) found existing ORs between TiB and prior- β grains can lead to these 6 variants during the $\beta\rightarrow\alpha$ transition, favouring those reducing structural mismatch and energy. Stacking faults may also help reduce the mismatch between TiB and the matrix (R. Banerjee, Collins, et al., n.d.; Cai et al., n.d.; Feng et al., n.d.), as observed by Otte et al. (J. Otte, Zou, et al., n.d.) in PBF-LB/M parts where stacking faults at the TiB and α -Ti interface enhanced structural continuity. The focus in literature is largely on TiB and α -titanium ORs, as α -titanium is the stable phase at room temperature, especially in CP-Ti without β stabilizers. This morphology significantly influences the ductility of $\alpha+\beta$ and near- β alloys (Y. Yang et al., n.d.). Feng et al. (Feng, Zhou, Jia, Meng, et al., 2006a) demonstrated semi-coherent interfaces of (100) TiB planes with both α -Ti and β -Ti matrices, as supported by Li et al. (D. Li et al., n.d.).

The literature presents conflicting findings on the alignment of TiB within AM components. Banerjee et al. (R. Banerjee et al., 2004a) observed notable differences in CP-Ti components alloyed with 2 wt.%B using DED. Eutectic TiB exhibited a coherent alignment with the neighbouring α phase, while proeutectoid TiB precipitates did not consistently align with the α matrix. This discrepancy is attributed to the distinct origins of proeutectoid TiB, forming directly from the liquid phase, as opposed to eutectic TiB, which crystallizes alongside the titanium matrix (R. Banerjee et al., 2004). Although TiB is expected to act as a potent nucleant for the α phase during the peritectoid reaction, Zhang et al. (K. Zhang et al., n.d.) found through re-indexed EBSD scans that TiB whiskers in Ti6Al4V parts modified by 0.5 or 1 wt.%B manufactured by DED lacked distinct ORs with the α matrix. This indicates that a consistent OR between TiB whiskers and the α matrix is not guaranteed, even in hypoeutectic

compositions where proeutectoid TiB is typically absent. The variations in orientation relationships observed in AMed titanium alloys are crucial to understand the effectiveness of load transfer from the matrix to the reinforcement. Further research is necessary to elucidate why these orientation relationships vary. This task is especially challenging in Ti6Al4V and other $\alpha+\beta$ alloys due to the dominant presence of the α phase, which complicates the identification of α domain origins (Hill et al., n.d.).

2.6.1.2 Hypoeutectic compositions

Bermingham et al. (M. J. Bermingham et al., 2018a) noted that adding small amounts of boron, ≈ 0.5 wt.% or less, alters solidification process of titanium, though the precise eutectic point might vary depending on the specific system. For example, Attar et al. (Attar et al., n.d.) found that CP-Ti components with 1.55 wt.%B underwent a hypoeutectic solidification process. In such cases, the composition of the melt pool is likely to stay hypoeutectic despite possible local composition variances. This means, as depicted in the binary phase diagram, indicated by a dotted line in Figure 2-48, that for hypoeutectic mixes, proeutectoid TiB no longer forms, and β -titanium is the first to crystallize (R. Banerjee et al., 2004).

Losert et al. (Losert et al., 1998) explained that the solidification pattern of an alloy is largely influenced by how quickly it solidifies. Rapid solidification causes the initially planar S/L front to become unstable, forming a pattern of cells that evolve from shallow to deep and eventually into dendrites with a branched structure. This instability is mainly attributed to constitutional supercooling, where solute rejection ahead of the solidification front occurs due to the solute being more soluble in the melt than in the solid. This leads to a compositional gradient, resulting in a gradient in crystallization temperature. If this temperature gradient exceeds the actual gradient at the S/L interface, the solidification front becomes unstable.

The solidification pattern of a molten alloy into a planar, cellular, or dendritic structure is influenced by both its composition and solidification conditions. CP-Ti and Ti6Al4V alloys tend to solidify dendritically, initially cooling at rates above 150°C/s , then slowing to around 30°C/s during the allotropic phase transformation (M. Bermingham et al., 2007). The introduction of boron further encourages dendritic growth, given low partitioning coefficient of boron in titanium (M. Bermingham et al., 2007; M. Bermingham, McDonald, Nogita, et al., n.d.). Regarding processing conditions, AM of metals typically features localized solidification within the molten pool, characterized by sharp thermal gradients and rapid cooling rates, favouring dendritic–columnar microstructures (Gudur et al., n.d.). However, cooling rates vary significantly across AM technologies, enabling controlled solidification in WAAM to achieve mixed equiaxed and columnar structures in Ti6Al4V, instead of purely dendritic ones (M. Bermingham, StJohn, et al., n.d.).

In hypoeutectic alloy compositions, titanium tends to form dendritic structures during solidification in most AM processes, a contrast to hypereutectic systems where TiB primarily crystallizes first (Ivasishin et al., 2008). Notably, in processes like PBF-LB/M, which feature exceptionally extreme cooling rates, solidification occurs under dynamic non-equilibrium conditions to reduce the effects of compositional undercooling, leading to microstructures

distinct from traditional casting methods (Alipour et al., n.d.). The solidification behaviour of any given composition is significantly influenced by the cooling rate, which varies with the specific AM process used (D. Gu et al., n.d.). Furthermore, the introduction of ceramic particles into the melt pool can disrupt and even reverse convection flows, affecting the upward growth of dendrites from the substrate and dragging them into the melt pool centre, thereby disrupting the formation of a regular dendritic structure (M. Bermingham, StJohn, et al., n.d.). The resulting microstructure of additively manufactured parts can also be altered by subsequent reheating, a phenomenon observed in hypereutectic alloy compositions.

In the solidification process of hypoeutectic systems, titanium solidifies into dendritic structures, as shown in Figure 2-49 (b), with boron reducing liquidus temperature of titanium. For instance, adding just 0.05 wt.% B to a Ti6Al4V alloy manufactured by WAAM lowers the solidification temperature by about 15–20 °C, from roughly 1679°C to 1660–1662°C (M. Bermingham, ..., et al., n.d.). As cooling progresses, boron, remaining in the liquid Ti, is gradually pushed out from the areas between growing β -Ti dendrites (or columnar grains) and eventually forms eutectic TiB in the remaining liquid pockets between the dendrites (Tamirisakandala, Bhat, Tiley, et al., n.d.). In metal AM, the formation of TiB particles in hypoeutectic compositions tends to occur between solidified columnar grains or in interdendritic spaces, aligning the eutectic TiB whiskers with the direction of growth (M. Bermingham, ..., et al., n.d.). This alignment is particularly noticeable in Ti6Al4V parts made by WAAM with added trace amounts of LaB₆ or elemental boron (M. Bermingham, ..., et al., n.d.). However, the microstructure can vary significantly with the cooling rates and processing conditions specific to each AM method, with WAAM typically leading to coarser features due to its relatively lower cooling rates compared to those in PBF-LB/M and direct energy DED-LB processes (Rashid et al., n.d.).

The final microstructure of Boron-modified parts mainly depends on the interaction between feedstock composition and processing parameters. A crucial design parameter is the eutectic composition, about 1.6 wt.%B. However, melt pool dynamics can alter the boron distribution, making local concentrations hyper- or hypo-eutectic, despite the nominal composition. Due to the short solidification time in AM, incomplete boron dissolution has been reported, as noted by Hu et al. (Y. Hu, Ning, et al., n.d.). Further experimental research on Boron-modified titanium and its alloys is detailed in Table 2-4. The last column in Table 2-4 includes information on the mechanical properties of B-modified Ti-based parts, discussed in Chapter 2.6.7.

Table 2-4 Experimental studies on adding Boron to AMed Titanium and its alloy parts.

Paper	AM parameters	Matrix	Source	Concentration	Microstructure	Properties
DED-LB:						
Banerjee et al.(R. Banerjee et al., 2004a)	Constant	CP-Ti	B particles	1 wt.% 2 wt.%	Bimodal distribution of primary and eutectic TiB Refined TiB size in AM compared to arc melted composites	Berkovich nanohardness: 130GPa Reduced modulus: 4.6GPa at 2 wt.%B
Banerjee et al.(R. Banerjee, Collins, et al., n.d.)	Constant with heat treatment	Ti6Al4V	B particles	2 wt.%	Primary and eutectic TiB No TiB precipitate coarsening post heat treatment Refined α/β microstructure Equiaxed α phase, not lath-type	—
Genç et al.(Genç et al., n.d.)	Constant	CP-Ti	B particles	2 wt.%	Stacking faults in B27 form of TiB Orientation relationship between TiB and α -Ti	—
Hu et al.(Y. Hu, Ning, et al., n.d.)	Evaluating laser power	CP-Ti	B particles (size: 2 μ m)	1.6 wt.%	Quasi-continuous network of primary and eutectic TiB at high laser power Balling defects from poor TiB wettability.	Increasing hardness with increasing power Improved hardness by 29.3% Reduced wear rate by one order of magnitude
Hu et al.(Y. Hu et al., 2017)	Evaluating laser power and z-axis increment	CP-Ti	B particles (size: 2 μ m)	1.6 wt.%	Flower-like structures with TiB growing from a central pore Higher power (energy density) increases density of both Ti and TMC Greater z-axis increment decreases density for both Ti and TMC	Hardness increases with laser power. Hardness remains almost constant with higher z-axis increments. TMC shows increased hardness. Ultimate compressive strength is higher. Ductility decreases under compression.
Hu et al.(Y. Hu, Cong, et al., n.d.)	Evaluating laser power	CP-Ti	B particles (size: 2 μ m)	1.6 wt.%	Quasi-continuous network of primary and eutectic TiB at high laser power	Higher yield strength under compression Higher ultimate strength under compression Lower ductility under compression Lower toughness under compression
Hu et al.(Y. Hu, Zhao, et al., n.d.)	Evaluating laser power	CP-Ti	B particles (size: 2 μ m)	1.6 wt.%	Quasi-continuous network of primary and eutectic TiB at high laser power	Improved hardness Increased compressive strength Reduced ductility at break
Huo et al.(Huo et al., 2023)	Initial optimization and 4h annealing at 950°C	Ti45Al8Nb	B, pre-alloyed	0.5 at.%	Lamellar colony grains refined from 75 to 45 μ m Non-uniformity factor reduced from 2.65 to 1.99 Phase transformation texture weakened from 58 to 20 TiB with orthogonal B27 structure	UTS increased by 8% Elongation at break increased by 51%
Rahman Rashid et al.(Rashid et al., n.d.)	Constant	Ti6Al4V	Amorphous B (size: 1 μ m)	0.05 wt.%	Discontinuous β -Ti grain boundaries Fine α laths replacing α' martensite needles Ultra-fine TiB	Increased hardness

Table 2-4 Continued.

Paper	AM parameters	Matrix	Source	Concentration	Microstructure	Properties
Xue et al.(A. Xue et al., n.d.)	Constant	Ti6Al4V	Amorphous B (size: 1 μm)	0.1 wt.% 0.2 wt.% 0.3 wt.%	Refined prior β -Ti grains Epitaxial prior β -Ti grains for B < 0.08 wt.% and alternating columnar and equiaxed dendrites for B > 0.17 wt.% Shorter grain boundary α and smaller colony α For low B content, TiB arranges between β dendrites with preferential orientation	Higher ultimate tensile strength Higher yield strength Lower ductility (deformation at break) Reduced anisotropy
Zhang et al.(K. Zhang et al., 2023)	Constant with annealing at 700°C for 2h	Ti6Al4V	B, pre-alloyed	0.05 wt.%	Mixed equiaxed/columnar grain structure More homogeneous and refined prior- β grains, width reduced from 314 μm to 76 μm Prior- β grain aspect ratio decreased from 3.8 to 2.7 More equiaxed and refined α grains, width reduced from 1.05 μm to 0.81 μm α grain aspect ratio decreased from 14.95 to 8.27 Randomly dispersed TiB traces	Tensile yield strength increased from 862MPa to 904MPa. UTS rose from 933 MPa to 982 MPa. Ductility remained almost the same, with elongation at break changing slightly from 10.2% to 10.0%. Tensile fracture surface showed a large, flat region of stable crack propagation. High-cycle fatigue life improved tenfold at 550MPa. Fatigue crack propagation profile was smooth. Fatigue crack propagation rates were nearly ten times faster.
Zhang et al.(K. Zhang et al., n.d.)	Constant with annealing at 700°C for 2h	Ti6Al4V	B, pre-alloyed	0.05 wt.% 0.5 wt.% 1.0 wt.%	Refined β grains: reduced from >400 μm to <90 μm Texture index of α phase decreased: from 36.4 to 1.7 Thinner α laths Suppressed grain boundary α : from 1.23 to 0.59 μm TiB growth and clustering: observed at 0.5 and 1 wt.%B	Improved tensile strength Less anisotropy in tension Lower ductility in tension Brittle failure above 0.05 wt.% B
PBF-EB: Mahbooba et al.(Mahbooba et al., 2017)	Constant	Ti6Al4V	B, pre-alloyed	0.25 wt.% 0.5 wt.% 1.0 wt.%	Reduced prior- β grain thickness Reduced α aspect ratio Reduced α lath area	Increased microhardness by 26% Increased elastic modulus by 9% Reduced ductility
WAAM: Bermingham et al.(M. Bermingham, Kent, et al., n.d.)	Constant with annealing at 480°C for 2h	Ti6Al4V	B, paint on substrate	0.05 wt.% 0.15 wt.%	Minor TiB fraction Reduced prior- β grain size from 1823 to 339 μm Reduced α aspect ratio by over 4 times Suppressed colony α Suppressed grain boundary α	No change in compressive properties of as-deposited parts 40% increase in compressive ductility post-heat treatment Reduced large-scale twinning Nanohardness increased to 27.00GPa

2.6.2 Alternative Sources of Boron Beyond Elemental Forms

In the context of additive manufacturing of titanium and titanium alloy components, a variety of boron-containing compounds have been investigated, such as chromium diboride (CrB_2) (N. Kang et al., 2016). However, the most extensively utilized sources of boron are titanium diboride (TiB_2), boron nitride (BN), lanthanum hexaboride (LaB_6), and boron carbide (B_4C). These materials will be examined in greater detail in the subsequent sections.

2.6.2.1 Titanium Diboride (TiB_2)

TiB_2 serves as an effective source of boron, contributing only boron as a microstructural modifier and titanium as the primary matrix component. Similar to most ceramic additives, TiB_2 exhibits a higher laser absorption coefficient compared to titanium, thereby enhancing energy (heat) absorption in laser-based additive manufacturing processes (Cai et al., n.d.). Despite being the most stable titanium boride within the Ti-B system, TiB_2 dissolves during printing and reacts with the titanium matrix to form TiB (Galvan et al., 2004), as described by the reaction:



Two mechanisms are proposed for the formation of TiB from TiB_2 . TiB can form either through the diffusion-driven removal of boron from TiB_2 into the titanium matrix, or through the melting of TiB_2 followed by in-situ TiB formation during solidification. According to Attar et al. (Attar et al., n.d.), both mechanisms are persuasive, but the diffusion of boron would be time-prohibitive compared to the rapid solidification times typical in PBF-LB/M processes, making the melting/solidification pathway more probable. In principle, in-situ TiB_2 might also form via the melting/solidification route. Notably, TiB_2 , with a lower enthalpy of formation ($-53.0 \text{ kcal/mol} \cong -221.8 \text{ kJ/mol}$), is thermodynamically more stable than TiB ($-28.0 \text{ kcal/mol} \cong -117.2 \text{ kJ/mol}$). Nevertheless, TiB tends to form instead of TiB_2 when the boron concentration in the reaction zone drops below 18-18.5% (J. Avila et al., n.d.; Bhuiyan et al., n.d.). Furthermore, Reaction 2.4 is highly exothermic, with a reaction enthalpy of -45 kJ/mol at 2300°C . For comparison, the heat of fusion for pure titanium is merely 15.45 kJ/mol , indicating that 3 mol of titanium can be melted as a result of the reaction between 1 mol of titanium and 1 mol of TiB_2 (Galvan et al., 2004). Occasionally, depending on the printing parameters and additive concentration, some TiB_2 may remain unreacted in the printed part, resulting in a hybrid ex-situ TiB_2 /in-situ TiB titanium matrix composite (TMC), as reported by Chen et al. (Y. Chen et al., 2017) and Galvan et al. (Galvan et al., 2004). However, in-situ grown reinforcements offer significant advantages over ex-situ ones. They ensure a more uniform distribution within the final part, and the size of the reinforcing phase can be controlled through processing conditions to be smaller than their ex-situ counterparts (Y. Hu, Ning, et al., n.d.). Moreover, the clean interface between in-situ reinforcement and the surrounding (Tjong & Mai, 2008) for efficient load transfer (Tjong & Mai, 2008). Another benefit of in-situ TMCs is that TiB is in thermodynamic equilibrium with the matrix, providing thermal stability and resistance to coarsening during heat treatment (R. Banerjee, Collins, et al., n.d.). Therefore, as discussed by Wang et al. (F. Wang et al., 2008), printing conditions should be optimized to ensure complete dissolution of primary borides, thus making the entire amount of boron available for microstructural refinement and the formation of secondary TiB. Examples of

experimental work on TiB_2 -modified systems are listed in Table 2-5. The mechanical behaviour of these systems, summarized in the last column of Table 2-5, is discussed in Chapter 2.6.7.

Table 2-5 Experimental studies on adding TiB₂ to AMed Titanium and its alloy parts.

Paper	AM parameters	Matrix	Source	Concentration	Microstructure	Properties
DED-LB:						
Galvan et al.(Galvan et al., 2004)	Process Window determination	CP-Ti	TiB ₂ particles (5-25 µm)	Ti: TiB ₂ = 2:1 Ti: TiB ₂ = 1:2 wt./wt.	Reduced unreacted TiB ₂ at lower scan speed Improved TiB ₂ dissolution at higher power Varied TiB forms at different laser power and concentration Strong interface between TiB and Ti matrix	TiB hardness: 30.7GPa TiB Young's modulus (indentation): 519GPa Hardness of eutectic layer: 7.5GPa Enhanced relative wear resistance
Wang et al.(F. Wang et al., 2008)	Assessment of laser power(with annealing or HIP for tensile testing)	Ti6Al4V	TiB ₂ particles (5-50 µm)	5 wt.% 10 wt.%	Unreacted TiB ₂ at low power Complete reaction at high power Coarser TiB precipitates with higher TiB ₂ addition Equiaxed α-phase and intergranular β-phase	Increased tensile strength post-annealing/HIP Increased yield strength post-annealing/HIP Microhardness rose from 340HV to 750HV Wear resistance improved; weight loss dropped from 0.35mm ³ to 0.008mm ³
PBF-LB/M:						
Attar et al.(Attar et al., n.d.)	Assessment of laser power and scan speed	CP-Ti	TiB ₂ particles (avg. 3.5-6 µm)	5 wt.%	99.5% relative density with optimal power/speed Fine eutectic TiB whiskers Refined α platelets Ti grains reduced from 2.1µm to 0.6µm in width and 15.3µm to 1.1µm in length	Hardness:402HV Higher compressive yield and ultimate strength Reduced ductility under compression
Attar et al.(Attar et al., 2015)	Different laser power	CP-Ti	TiB ₂ particles	1.5 wt.%	α matrix instead of α' martensite Both fine and coarse TiB Precise lattice geometry	Enhanced compressive yield strength Reduced ductility under compression
Attar et al.(Attar, Bönisch, Calin, Zhang, Zhuravleva, et al., 2014)	Constant	CP-Ti	TiB ₂ particles (avg. 3.5-6 µm)	5 wt.%	99.5% relative density Refined TiB precipitates compared to cast samples Refined α grains by 50% compared to cast samples TiB arranged in colonies Intragranular TiB	Harder than powder metallurgy samples, yet similar hardness to cast samples Similar compressive behaviour to cast samples, but with higher yield strength Compressive failure mainly due to microcracks Higher tensile modulus than powder metallurgy samples
Batalha et al.(Batalha et al., 2022a)	Constant	Ti35Nb7Zr5Ta	TiB ₂ particles (d ₅₀ = 4 µm)	1 wt.%	TiB precipitates in β matrix Porosity of 98.7% with LOF pores present Refined β columnar-dendritic crystals Increase in equiaxed grains from 327µm (length) and 72µm (width) to 58µm (length) and 49µm (width)	Tensile modulus similar to cast samples Compressive tests stopped at 60% strain without failure. Compressive strength increased by 15%. Compressive Young's modulus remained nearly constant at 46GPa.
Cai et al.(Cai et al., n.d.)	Constant after initial optimization of parameters	Ti6Al4V	TiB ₂ particles (d ₅₀ = 2.71 µm)	1 wt.% 2 wt.% 3 wt.%	High density with some metallurgical and inter-layer pores Larger and deeper melt pool TiB precipitates in α-Ti matrix with intergranular β-Ti traces Refined α-Ti laths Coarser microstructure with increased TiB ₂ addition	Nanohardness and Young's modulus rise with higher TiB ₂ concentration Nanohardness increased from 4.38 to 6.00GPa Young's modulus increased from 131 to 143GPa Average friction coefficient decreased from 0.44 to 0.35 at 60N load Wear mass loss decreased from 4.4 to 2.2mg

Table 2-5 Continued.

Paper	AM parameters	Matrix	Source	Concentration	Microstructure	Properties
Chen et al.(Y. Chen et al., 2017)	Constant	CP-Ti	TiB ₂ particles (avg. 3.5-6 μm)	5 wt.%	Fine TiB precipitates Minor traces of unreacted TiB ₂ Refined α-Ti grains from 2μm wide and 16μm long to 0.5μm wide and 1μm long	Enhanced corrosion resistance in Hank's solution
Dong et al.(Dong et al., 2020)	VED assessment via laser power and scan speed	Modified hydrogenated-dehydrogenated (HDH) Ti	TiB ₂ particles (d ₅₀ = 1.3 μm)	0.5 wt.% 1 wt.% 2 wt.%	For 0.5 wt.% of TiB ₂ , max. density is 99.3% at intermediate VED The α/α' laths become more equiaxed and refined from around 10μm to 1.11μm TiB precipitates coarsen and aggregate as TiB ₂ concentration increases	Higher TiB ₂ addition boosts tensile and compressive strength. Higher TiB ₂ addition reduces tensile and compressive plasticity; 0.5 wt.% TiB ₂ is optimal. Hardness increased from 298HV to 411HV.
Patil et al.(A. Patil et al., n.d.)	Constant	Ti6Al4V	TiB ₂ particles (avg. 11 μm)	0.2 wt.% 0.5 wt.% 1 wt.% 1.5 wt.% 2 wt.%	Decreased density with no clear trend on TiB ₂ addition Smaller martensitic laths with increasing TiB ₂ addition Transition from martensitic to bimodal structure (equiaxed α and colony α) at high TiB ₂ addition	Hardness increases linearly with TiB ₂ addition Hardness rose from 383HV to 477HV Coefficient of friction remains nearly constant Wear resistance improved
Singh et al.(N. Singh et al., 2021)	Constant	Ti6Al7Nb	TiB ₂ particles (<10 μm)	1.5 wt.% 3.0 wt.%	Density > 98.5% α' martensite transformed to α/α' Primary TiB served as nucleation site for prior-β Refined microstructure with increased TiB ₂ Quasi-continuous TiB network at 3 wt.%TiB ₂	Hardness increased from 395HV to 569HV Yield strength under compression increased from 1029MPa to 1633MPa Lower corrosion current in simulated body fluid compared to wrought Ti6Al4V, regardless of TiB ₂ addition.
Su et al.(Su et al., 2020)	VED assessment via scan speed	Ti6Al4V	TiB ₂ particles (3-5 μm)	1 wt.% 3 wt.%	Higher TiB ₂ addition requires lower printing speed (higher energy density). Increased energy density enhances density. TiB tends to form at grain boundaries. Higher TiB ₂ refines Ti6Al4V microstructure. Increased TiB ₂ results in coarser TiB.	For Ti6Al4V, microhardness increases with higher energy density. For composites, microhardness initially increases, then decreases with higher energy density. Hardness increased from 440HV to 524HV. Friction coefficient reduced from 0.44 to 0.35 at maximum energy density. Wear resistance increased.
Zhou et al.(Z. Zhou et al., 2023a)	Constant Different heat treatments after printing	Ti6Al4V	TiB ₂ particles (100-200 nm)	1.88 wt.%	Narrower columnar β grains and finer α/α' laths in as-built composites Clustered TiB needles in as-built composites Heat treatment transforms microstructure to lamellar, bilamellar, or bimodal TiB migrated to molten pool boundaries in lamellar and bilamellar structures Uniform TiB distribution in bimodal microstructure	For as-built parts, UTS increased from 844MPa to 1095MPa at 400°C, and from 512MPa to 522MPa at 600°C, showing a reduced strengthening effect. As-built parts of TMCs have superior creep resistance compared to Ti6Al4V Heat treatment further enhanced the creep resistance of TMCs. The steady-state creep rate of bimodal microstructure decreased by 40%, and rupture time at 250MPa increased by 29% compared to as-built TMCs.

2.6.2.2 Boron Nitride (BN)

BN serves as a typical precursor for boron. As a standalone material, BN is characterized as an insulating ceramic with excellent thermal conductivity and a high melting point of 2973°C. Nevertheless, unless it is in a nanostructured form (Chao et al., n.d.), BN exhibits limited mechanical strength and hardness, along with poor oxidation resistance (Ding et al., 2005). Despite the existence of cubic BN (Minasyan et al., 2019), the hexagonal form is predominantly utilized in the additive manufacturing of titanium matrix composites (TMCs). Under equilibrium conditions, a variety of reactions can occur within the Ti-BN system, contingent upon the stoichiometry of the system (J. Avila et al., n.d.; Borisova et al., 1984):



The probability of each reaction, indicated by asterisks, has been evaluated based on the reaction enthalpies documented by Borisova et al. (Borisova et al., 1984). Thermodynamic analysis suggests that within the temperature range of 500 to 2000 K, the most likely outcome is the formation of a composite of titanium borides and nitrides, as described by Reactions 2.7 and 2.9 (J. Avila et al., n.d.; Borisova et al., 1984). It has been established that TiB_2 is thermodynamically more stable compared to TiB , implying that TiB_2 would initially form from the reaction between boron and titanium in the vicinity of BN particles. However, as previously discussed, TiB_2 is prone to conversion to TiB via Reaction 2.4 (J. Avila et al., n.d.; Bhuiyan et al., n.d.).

While reactions 2.5 to 2.9 refer to equilibrium conditions, in metal additive manufacturing, the high energy density supplied by the incident beam (or other energy source) and the rapid cooling rates promote non-equilibrium reactions (D. D. Gu et al., 2012). This results in the stabilization of metastable phases and polymorphs, with kinetic-sensitive processes (such as solid-state diffusion) being influenced or restricted. Such conditions may cause deviations from the equilibrium interactions between BN and the surrounding metal matrix. When the energy delivered to the melt pool exceeds a certain threshold, BN decomposes into nitrogen and boron within the liquid metal (J. Otte, Zou, et al., n.d.). Numerous studies report selective depletion of nitrogen during printing, as confirmed by elemental analysis of printed parts, where nitrogen content is significantly lower than boron, despite a 1:1 molar ratio addition of BN (Chao et al., n.d.; J. Otte, Zou, et al., n.d.; L. Wang et al., 2023). Given small atomic radius of nitrogen (0.75Å), it rapidly diffuses away from the original BN particles (Pantawane et al., 2020). The solid solubility of nitrogen in titanium is 8 wt.% at 1000°C but decreases to 0.1 wt.% at 100°C (J. Otte, Zou, et al., n.d.). For relatively low concentrations below 8 wt.%, nitrogen likely becomes interstitial at high temperatures and remains trapped as solute atoms in the matrix due to fast cooling [30]. However, if the local nitrogen concentration exceeds the solubility limit, titanium nitrides can form. While TiN is the equilibrium product, Avila and Bandyopadhyay (J. Avila et al., n.d.) also observed metastable titanium nitrides, such as $\text{TiN}_{0.176}$, in DED-LB

parts with 3 or 6 wt.% BN in CP-Ti matrix. For higher BN concentrations of 5 and 15 wt.%, $\text{Ti}_3\text{N}_{1.29}$ was the predominant phase in DED-LB coatings, followed by TiB and TiN in Ti6Al4V matrix, as studied by Das et al. (Das, Balla, et al., n.d.; Das, Bhattacharya, et al., n.d.). Since TiN has a higher melting point (3600°C) than TiB, TiN solidifies first from the liquid during cooling. The remaining liquid, now depleted in nitrogen and enriched in boron, facilitates the growth of TiB and non-equilibrium titanium nitrides (Das, Balla, et al., n.d.).

Several studies have reported the presence of partially unreacted BN particles in printed parts (J. Otte, Zou, et al., n.d.). This may result from insufficient energy delivery to complete BN dissolution or suboptimal processing parameters. Otte et al. (J. Otte, Zou, et al., n.d.) observed that, even with constant energy density, the microstructure varies if laser power and scanning speed are simultaneously increased. Specifically, higher melt pool temperatures, achieved by increased laser power, favour BN dissolution. Consequently, Otte et al. (J. Otte, Soro, et al., n.d.; J. Otte, Zou, et al., n.d.) recommended a laser power of 180 W or more to ensure BN dissolution in PBF-LB/M parts containing 1 wt.% hexagonal BN nanoplatelets. However, the minimum laser power needed for complete BN dissolution cannot be generalized, as it depends on various factors, including BN particle size, BN content added, AM technology, and the specific printing equipment used. Kinetic factors may also influence outcomes, as high cooling rates might prematurely halt reactions between BN and titanium (J. Avila et al., n.d.). The persistence of (partly) unreacted BN particles is thus more likely in regions with limited thermal cycling and the highest cooling rates, such as the perimeter of each layer and the top of the part (Chao et al., n.d.; J. Otte, Zou, et al., n.d.).

More details about experiments with BN can be found in Table 2-6, which also includes a review of the mechanical properties of B4C-modified parts. Additional information on mechanical behaviour is in Chapter 2.6.7.

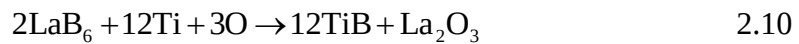
Table 2-6 Experimental studies on adding BN to AMed Titanium and its alloy parts.

Paper	AM parameters	Matrix	Source	Concentration	Microstructure	Properties
DED-LB:						
Avila and Bandyopadhyay(J. Avila et al., n.d.)	Specific to each composition	CP-Ti	Hexagonal BN (size <74 μm)	3 wt.% 6 wt.%	Transformation from α' to α -Ti TiB growth in α -Ti matrix, with residual BN, TiN, and TiN0.176 phases Coarser microstructure post-heat treatment	Early-stage oxidation rate decreased Long-term oxidation rate halved Mass loss reduced by 35.5% Hardness increased from 157HV to 585HV Hardness improved after heat treatment Compressive yield strength increased by 50% Ultimate compressive strength rose by 40% Compressive ductility slightly decreased Hardness increased from 342HV to 433HV
Chao et al.(Chao et al., n.d.)	Constant	Ti6Al4V	BN nanotubes	0.1 wt.% 0.4 wt.%	Density over 99.9% Equiaxed, refined prior- β grains reduced from 337 μm to 9 μm α lath aspect ratio reduced from over 10 to 2.1, with thickness 485–550 nm 13% retained β phase fraction Nanosized TiB whiskers at prior- β grain boundaries Some whiskers within prior- β grains Weakened texture	
Das et al.(Das, Bhattacharya, et al., n.d.)	VED assessment via laser power and scan speed	Ti6Al4V	Hexagonal BN (size: 0.5–2 μm)	5 wt.% 15 wt.%	Defect-free coating on CP-Ti Strong interface bonding Thicker coating at 15 wt.% BN than at 5 wt.% Flowery/dendritic TiN and fine rod-like TiB Out-of-equilibrium phases present Finer precipitates at lower BN loading Finer precipitates at lower energy density	Hardness increased from 604HV (5 wt.%) to 877HV (10 wt.%). Young's modulus rose from 184GPa (5 wt.%) to 204GPa (10 wt.%). Lowest wear rate in simulated body fluid Comparable bioactivity.
PBF-LB/M:						
Minasyan et al.(Minasyan et al., 2019)	Evaluating laser power	CP-Ti	Cubic BN (size: 30–70 μm)	5 wt.% 15 wt.%	Density ranges from 95–99% at 5 wt.% BN and 93% at 15 wt.% BN High amount of unreacted BN Weak BN-Ti bonding at low laser power	Enhanced hardness for increasing BN addition
Otte et al.(J. Otte, Zou, et al., n.d.)	Parameter optimisation with heat treatment	CP-Ti	Hexagonal BN nanoplatelets (65–75 nm size; width <100 nm; thickness <10 nm)	2.5 vol.%	Predominantly martensitic phases with refined grains Minimal TiB precipitates and residual BN below 140W Heat treatment increased TiB diameter from 26 nm to 43 nm and length from 5.1 μm to 17.3 μm	Tensile modulus increased by 26.5% Yield strength increased by 79.2% Ultimate tensile strength increased by 57.8% Ductility decreased but remained above 5% Hardness increased by 120%
Otte et al.(J. Otte, Soro, et al., n.d.)	Parameter optimisation for lattice structures with heat treatment	CP-Ti	BN nanoparticles (size: 65–75 nm)	2 vol.%	Density over 99%, with a maximum of 99.67% Refined prior- β grains α phase refined from coarse grains/laths to fine acicular α TiB nanowhiskers Post-heat treatment: nearly equiaxed α grains of 3.6 μm	Compressive yield strength doubled to 1123MPa Compressive modulus up to 2.5GPa Compressive strength up to 62.3MPa Elastic strain limit of 2.5%
Wang et al.(L. Wang et al., 2023)	Constant	Ti6Al4V	Hexagonal BN (size <10 μm)	0.5 wt.%	Mixed grain structure with alternating bands of columnar and equiaxed prior- β Ti grains (75% columnar) Columnar grains: 10 μm wide, 53 μm long Equiaxed grains: 7 μm in size TiB located mainly at prior- β grain boundaries	Ultimate compressive strength increased Compressive yield strength: 1648MPa Plastic strain: 6.5% Hardness: 645HV in equiaxed bands Hardness: 557HV in columnar bands

2.6.2.3 Lanthanum Hexaboride (LaB₆)

In the scientific literature, while TiB₂ and BN are the more frequently studied boron precursors, other non-elemental boron sources, such as lanthanum hexaboride (LaB₆), have also been explored (M. Bermingham, ..., et al., n.d.). Rare earth elements, including lanthanum and yttrium, have been shown to effectively refine the grain size of titanium alloys when used in minor amounts (Samsonov et al., 1970). Furthermore, these elements offer the benefit of reducing the dissolved oxygen concentration in titanium through a 'scavenging' mechanism (Y. Liu et al., 2012; M. Yan et al., 2015). This is attributed to their higher chemical affinity for oxygen compared to titanium (Y. F. Yang et al., 2014). Consequently, this scavenging effect could potentially increase the tolerance of titanium alloys to oxygen, facilitating the use of more economical titanium powders for additive manufacturing and enabling advancements in printing technologies that do not require an inert gas or vacuum environment (M. Bermingham, ..., et al., n.d.).

LaB₆, similar to boron nitride, exhibits a higher laser absorption coefficient compared to titanium (D. He et al., 2023). Upon mixing with titanium in the presence of oxygen, LaB₆ undergoes decomposition and reacts as described in (M. Bermingham, ..., et al., n.d.):



This reaction process concurrently facilitates the elimination of dissolved oxygen through the formation of nanoscale La₂O₃, which remains uniformly distributed within the matrix, and results in the production of TiB, thereby refining the microstructure of titanium.

Bermingham et al. (M. Bermingham, ..., et al., n.d.) validated the efficacy of LaB₆ in WAAM. The LaB₆ was incorporated within the tolerance limits set by ASTM F2924 (ASTM International, 2021), ensuring the concentration of lanthanum (La) and boron each remained below 0.10 wt.%. A notable outcome of adding LaB₆ was the alteration in the aspect ratio of the deposited bead compared to pure Ti6Al4V and Ti6Al4V modified with 0.05 wt.%B. Specifically, the bead width decreased significantly while the height increased, leading to undulations and build-up instabilities during printing. This change in bead aspect ratio with LaB₆, but not with elemental boron, suggested that the presence of lanthanum was primarily responsible for this effect. Lanthanum is known for its strong surface activity, having a lower surface tension than titanium and reducing the liquid surface tension in various alloys. However, during WAAM, lanthanum tends to become 'trapped' by oxygen, as per Reaction 2.10, which significantly limits the amount of lanthanum available to alter the surface energy of alloy. Concurrently, Reaction 2.10 also significantly reduces the dissolved oxygen, which typically decreases the surface tension in many metals. Furthermore, Bermingham et al. (M. Bermingham, ..., et al., n.d.) hypothesized that while the surface tension of molten metals generally decreases with rising temperature, lanthanum might invert the surface tension temperature coefficient of Ti6Al4V (the 'Heiple-Roper effect'). This inversion could shift the Marangoni flow direction from outward to inward, thereby preventing the melt pool from spreading laterally. Bermingham et al. (M. Bermingham, ..., et al., n.d.) also examined the

mechanisms underlying the formation of La_2O_3 . Given that lanthanum has a solubility of approximately 8 wt.% in β -titanium but nearly zero in α -titanium, Yang et al. (Z. Yang et al., 2008) hypothesized that La_2O_3 should emerge during the $\beta \rightarrow \alpha$ transformation, rather than immediately following the decomposition of LaB_6 . While this mechanism remains conceivable, Bermingham et al. (M. Bermingham, ..., et al., n.d.) advocated for the hypothesis that La_2O_3 forms during the decomposition of LaB_6 . They noted that thermodynamic factors, particularly Gibbs free energy considerations, support this scenario. Additionally, cooling curves of LaB_6 -modified Ti6Al4V obtained during WAAM did not reveal any reactions indicative of La_2O_3 formation (or any La-containing intermetallics). Furthermore, Bermingham et al. (M. Bermingham, ..., et al., n.d.) observed that La_2O_3 particles are uniformly distributed in the alloy within LaB_6 TMCs, which would be improbable if La_2O_3 formed during the $\beta \rightarrow \alpha$ transformation. He et al. (D. He et al., 2023) reached similar conclusions regarding the impact of LaB_6 on Ti6Al4V components produced by PBF-LB/M. The fine and homogeneous dispersion of La_2O_3 particles, contrasted with the segregated distribution of TiB, reinforced the hypothesis that LaB_6 decomposition and La_2O_3 formation occur simultaneously, as previously suggested by Bermingham et al. (M. Bermingham, ..., et al., n.d.). Despite the high laser absorption coefficient of LaB_6 , He et al. (D. He et al., 2023) reported the presence of unreacted LaB_6 particles when the LaB_6 content reached 3 wt.%. This phenomenon was attributed to the tendency of LaB_6 particles to form large agglomerates at higher concentrations. These unreacted LaB_6 particles subsequently acted as heterogeneous nucleation sites.

Further details on experiments with LaB_6 can be found in Table 2-7. The last column of Table 2-7 also reviews the mechanical properties of LaB_6 -modified parts. Chapter 2.6.7 is offering additional insights into mechanical behaviour.

Table 2-7 Experimental studies on adding LaB₆ to AMed Titanium and its alloy parts.

Paper	AM parameters	Matrix	Source	Concentration	Microstructure	Properties
DED-LB:						
Huang et al.(D. Huang et al., n.d.)	Constant	β-solidifying TiAl alloy	LaB ₆ nanoparticles (100 nm)	0.2 wt.% 0.5 wt.% 1 wt.% 2 wt.%	Nearly lamellar microstructure converted to duplex Reduced texture Refined β grains Lower cracking tendency Oxygen removal via La ₂ O ₃ formation Ribbon-like TiB arrangement Retained β ₀ phase Increased porosity above 0.5 wt.% LaB ₆	Optimized compressive properties (strength, yield strength, deformation at break) with 0.5 wt.% addition Tensile properties at 0.5 wt.% are comparable to castings.
PBF-LB/M:						
He et al.(D. He et al., 2023a)	Constant	Ti6Al4V	LaB ₆ particles (avg. 7.4 μm)	0.5 wt.% 1 wt.% 3 wt.%	Reduced density to 96.5% Uniform distribution of La ₂ O ₃ TiB transitions from discrete needles to dendritic, and finally to cell-like structures Dislocation pile-up around precipitates	Microhardness increased by 35.7% Tensile strength increased by 14.5% Wear volume down by 47.5% Ductility down by 37.2%
WAAM:						
Bermingham et al.(M. Bermingham, ..., et al., n.d.)	Constant with HIP under 150 MPa at 920°C for 4h	Ti6Al4V	LaB ₆ , paint on build surface B, paint on surface	Within ASTM F2924-14 limits	Significantly reduced bead aspect ratio and build-up instabilities Large, highly oriented TiB crystals La ₂ O ₃ undetectable, below XRD threshold	Tensile strength improved by 10% Significantly reduced ductility Pronounced anisotropic effects

2.6.2.4 Boron Carbide (B₄C)

Boron carbide (B₄C) has gathered significant interest due to its ability to contribute both boron and carbon, facilitating the formation of highly stable and extremely hard reinforcements such as TiB and TiC. However, due to its elevated melting point of 2350°C (Y. Zhang et al., 2011), B₄C is unlikely to fully melt or dissolve during printing processes. Residual unmelted and unreacted B₄C particles are frequently observed even in PBF-LB/M techniques, despite the localized high energy input from the laser beam and the relatively high laser absorption coefficient of B₄C (C. Han et al., 2020). Another complication in laser-based manufacturing processes is the low thermal diffusivity of B₄C. Although B₄C particles are capable of absorbing substantial energy from the laser, they lack the ability to effectively transfer this absorbed heat to the surrounding metal particles. When B₄C-coated metal particles are used as composite feedstock, the B₄C surface layer can act as a thermal barrier, inhibiting the transfer of energy to the metal and preventing its melting (Fereiduni et al., 2019).

Given its remarkable thermal stability, B₄C tends to dissolve in the melt pool instead of melting. This dissolution process is facilitated by the excellent compatibility between liquid titanium and B₄C, which can be understood as the diffusion of boron and carbon atoms from solid B₄C into the liquid titanium. Although theoretically, titanium atoms could also diffuse from the liquid titanium into the solid B₄C, the rate of solid-state diffusion is significantly slower than that of liquid-state diffusion. The convective flow within the melt pool promotes the dissolution of B₄C, and, predictably, complete dissolution is more readily achieved with smaller particles (Fereiduni et al., 2019; C. Han et al., 2020). Upon dissolution, B₄C reacts with titanium, resulting in the formation of TiB or TiB₂ and TiC. The reactions proceed according to the following mechanisms (Tjong & Ma, 2000):



Nevertheless, the presence of TiB₂ in literature is uncommon, with only a few examples such as the PBF-EB components investigated by Tao et al. (Tao, Yao, Zhang, et al., 2018), and the DED-LB (laser-clad) coatings studied by Tian et al. (Tian et al., n.d.). This rarity is due to the tendency of TiB₂ to react with the titanium matrix, resulting in the formation of TiB as depicted in Reaction 2.4. Furthermore, based on the thermodynamic calculations conducted by Tian et al. (Tian et al., n.d.), both the formation enthalpy and Gibbs free energy for these reactions are negative. However, the Gibbs free energy for Reaction 2.11 is lower, i.e., more negative, than that for Reaction 2.12, up to at least 2200K. This suggests that TiB is more likely to form than TiB₂ under these conditions.

In contrast to TiB, which typically develops in elongated prismatic or needle-like shapes, TiC tends to form equiaxed particles due to its BCC structure. Nonetheless, dendritic formations have also been reported in regions with high carbon content (Z. Wang et al., 2023; Yi et al., n.d.). Similar to TiB, TiC possesses a density and coefficient of thermal expansion comparable to those of titanium, thereby stimulating interest in TiC-reinforced and (TiC+TiB)-reinforced

titanium matrix composites (Z. Wang et al., 2023). The study by Zhang et al. (Y. Zhang et al., 2011) on DED-LB fabricated parts demonstrated a clean interface between the Ti6Al4V matrix and the in-situ formed TiB and TiC reinforcements. In contrast, the interface with unreacted B₄C particles was weak, leading to brittle failure under tensile loading at a comparatively low stress level of 815 MPa.

To clarify the influence of B₄C content added, Pouzet et al. (Pouzet et al., 2016) fabricated (TiB+TiC)-reinforced Ti6Al4V thin walls using DED-LB, starting with varying concentrations of B₄C. EBSD analysis of the fabricated parts revealed that the addition of B₄C resulted in prior β -titanium grains becoming nearly equiaxed, with a notable decrease in grain size from 150 μ m in base Ti6Al4V to 30 μ m in composites containing 3 wt.% B₄C. At ambient temperature, all samples displayed an α/β Widmanstätten titanium matrix with TiB whiskers uniformly distributed in a network. Additionally, primary TiB prismatic crystals were observed in the parts containing 3 wt.% B₄C. However, aside from the occasional formation of primary TiB precipitates, the microstructure was similar between samples with 3 wt.% B₄C (hypereutectic, equivalent to 2.34 wt.%B) and those with 1.5 wt.% B₄C (hypoeutectic). This observed anomaly was potentially due to a shift in the Ti-B eutectic point to higher concentrations caused by the high cooling rate, or a lack of convection-driven chemical homogenization in the melt pool. In contrast, TiC precipitates were nearly undetectable, likely due to the progressive dissolution of C in the α -phase. However, the maximum solubility of C in α -titanium was achieved at 1.5 wt.% B₄C, as indicated by the hardness measurements. Since the hardness of the printed parts was determined by C-driven solution hardening, the hardness increased significantly with the addition of B₄C from 0 to 1.5 wt.% but remained nearly constant at 3 wt.%. Han et al. (C. Han et al., 2020) investigated the incorporation of B₄C into titanium in varying proportions during PBF-LB/M fabrication, noting the atomic ratio of B:C in B₄C is 4:1. This implies that with an increase in the B₄C weight fraction within the composite, the atomic concentration of boron rises more promptly than that of carbon. Their findings indicated that a mere 1 wt.% addition of B₄C transformed the standard lath-like microstructure of PBF-LB/M titanium into a dendritic form. With further increments in B₄C content from 2 to 5 wt.%, the microstructure evolved from dendritic to a cellular hybrid. At 5 wt.% B₄C, primary TiB crystals were found alongside nanoscale eutectic TiB+TiC structures, with TiC particles mechanically interlocked on TiB whiskers. These precipitates converged at the α -titanium grain boundaries, forming a cellular network. However, at higher B₄C concentrations, partial unreacted B₄C and significant cracking were observed, which reduced the density of printed parts and impaired their tensile strength. The optimal tensile strength was achieved at 1 wt.% B₄C, but this enhancement was coupled with a significant reduction in ductility.

Processing with an electron beam presents significant challenges due to potential charge accumulation caused by the presence of B₄C. One effective strategy involves incorporating CaF₂ and other fluxes to protect and bond the feedstock powders. Utilizing this approach, Yun et al. (Yun et al., 2004) produced five TMC coatings through electron beam irradiation using various ceramic powders, including TiC, Ti+C, TiB₂, Ti+B₄C, and TiC+TiB₂, with CaF₂ flux added at 50 wt.%. Comparative analysis of these coatings revealed that the composite

containing B_4C exhibited the highest hardness, maintained even at elevated temperatures, attributed to the substantial volume fraction of TiB and TiC uniformly distributed within the martensitic matrix. Similarly, Lenivtseva et al. (Lenivtseva et al., 2016) utilized CaF_2 (40 wt.%) and LiF (10 wt.%) to inhibit oxidation in non-vacuum electron beam cladding, a process analogous to DED-EB, and found that in-situ TiB+TiC reinforced titanium claddings exhibited superior wear resistance compared to CP-Ti. To avoid the use of fluxes that might evaporate and cause high voltage discharge, Tao et al. (Tao, Yao, Zhang, et al., 2018) pre-sintered a mixture of CP-Ti and B_4C powders using SPS, followed by surface reprocessing via PBF-EB. During the SPS pre-treatment, the temperature was maintained below the minimum inter-diffusion reaction temperature between Titanium and B_4C , allowing some titanium particles to pre-sinter without any reaction or diffusion. PBF-EB parts processed with minimal energy input contained unreacted B_4C particles, typically surrounded by TiB_2 whiskers radiating from the central B_4C . This unique microstructure resulted from the slow diffusion of boron from B_4C , promoting local boron enrichment and the formation of TiB_2 rather than TiB. TiB_2 persisted in the final part due to rapid cooling, which prevented further reaction with titanium. As the energy input increased, B_4C fully dissolved and reacted with titanium, producing TiB whiskers and TiC particles. However, the reduced cooling rate and higher local temperature encouraged the growth of larger TiB precipitates.

The findings reported by Tao et al. (Tao, Yao, Zhang, et al., 2018) align with the microstructural evolution previously detailed by Xia et al. (Xia et al., 2017) for PBF-LB/M components. In both studies, an incremental increase in laser power, and consequently energy input, facilitated the Ti- B_4C diffusion/reaction process and encouraged the formation of larger precipitates. However, a notable difference was observed in the absence of TiB_2 crystals in the PBF-LB/M parts, which can be attributed to variations in convection flow and cooling rates within the melt pool. In Tao et al.'s study (Tao, Yao, Zhang, et al., 2018), depth-sensing nanoindentation of PBF-EB components revealed that samples subjected to intermediate energy input exhibited the highest hardness and the highest reduced elastic modulus. Similarly, these samples demonstrated superior wear resistance and the lowest coefficient of friction. These enhanced mechanical properties were ascribed to the complete dissolution/reaction of B_4C and the development of fine TiB precipitates (Tao, Yao, Zhang, et al., 2018).

Additional details about experiments with B_4C are in Table 2-8, which also summarizes the mechanical properties of B_4C -modified parts. Further insights into the mechanical behaviour can be found in Chapter 2.6.7.

Table 2-8 Experimental studies on adding B₄C to AMed Titanium and its alloy parts.

Paper	AM parameters	Matrix	Source	Concentration	Microstructure	Properties
DED-LB:						
Pouzet et al.(Pouzet et al., n.d.)	Assessment of scanning speed, laser power O ₂ concentration, and 600°C annealing for 2h	Ti6Al4V	B ₄ C particles (25-45 μm)	0.5 wt.% 1.5 wt.% 3 wt.%	Minor unreacted B ₄ C Prismatic and needle-like TiB Almost complete dissolution of C in Ti with up to 1.5 wt.%B ₄ C Equiaxed prior β-Ti Refined prior β-Ti from 150μm to 30μm at 3 wt.%B ₄ C Similar microstructure for 1.5 and 3 wt.%B ₄ C	Microhardness is similar for 1.5 wt.% and 3 wt.%B ₄ C addition Stiffness (dynamic resonant method) is similar for 1.5 wt.% and 3 wt.%B ₄ C addition Tensile ductility decreases with 1.5 wt.%B ₄ C addition
Zhang et al.(Y. Zhang et al., 2011)	Constant Annealing at 600°C for 2h	Ti6Al4V	B ₄ C particles (30-45 μm)	5 wt.%	Unreacted B ₄ C with surrounding precipitates Presence of TiC, TiB (prismatic and needle-like), and traces of TiB ₂ Refined α/β-Ti phases	Brittle failure with an ultimate tensile strength of 815 MPa at room temperature
PBF-LB/M:						
Fereiduni et al.(Fereiduni et al., 2019a)	VED evaluation through laser power	Ti6Al4V	B ₄ C particles	5 wt.%	Primary TiB, eutectic TiB, TiC, ternary TiB, TiC, and β-Ti β-Ti evolving to martensitic α'-Ti Unreacted B ₄ C B ₄ C dissolving rather than melting	Microhardness increased by 30-50% based on laser energy
Han et al.(C. Han et al., 2020)	Constant after initial optimization of parameters	CP-Ti	Nanosized B ₄ C particles	1 wt.% 2 wt.% 3 wt.% 5 wt.%	Microstructure changes from lath-type to dendritic to hybrid cellular Presence of primary TiB, eutectic TiB, and TiC TiC mechanically locked onto TiB Coalesced TiB and TiC at α grain boundaries Partly unreacted B ₄ C at high concentrations Cracks observed at high concentrations	At 1 wt.%, ultimate tensile strength increased by 62.4%, yield strength by 49.2%, and Young's modulus by 15.3%. Ductility decreased from 26.4% to 0.6%.
Tian et al.(Tian et al., n.d.)	Evaluating laser power (laser surface glazing)	CP-Ti	B ₄ C particles (avg: 10 μm)	50 wt.%	TiB, TiB ₂ and TiC precipitates Coarser precipitates form at slower speeds	Gradual decrease in microhardness towards the substrate Lower coefficient of friction Enhanced wear resistance
Xia et al.(Xia et al., 2017)	Evaluating laser power	CP-Ti	B ₄ C particles (avg: 5 μm)	5 wt.%	For low energy input: unreacted B ₄ C with TiB whiskers, TiB, and TiC. For high energy input: coarse TiB.	Reducing hardness with higher energy input Microhardness of 577.1HV at minimum energy
Xia et al.(Xia et al., n.d.)	Evaluating scan speed	CP-Ti	B ₄ C particles (avg: 3 μm)	5 wt.%	Reduced density (98.9% to 89.2%) and LOF pores with higher scan speed Coarse precipitates at low scan speed Unreacted B ₄ C	Microhardness peaks at 459.3HV at 1 m/s. Dynamic friction coefficient drops to 0.09 at 1.4 m/s. Minimum wear rate of 0.85×10 ⁻¹³ m ³ /m at 1 m/s.
Electron-beam AM						
Lenivtseva et al.(Yi et al., n.d.)	Evaluating beam current (electron beam cladding)	CP-Ti	B ₄ C Fluxes: 40 wt.% CaF ₂ ; 10 wt.% LiF	20 wt.%	Unreacted B ₄ C, mainly in lower layers TiB whiskers TiC dendrites	Enhanced wear resistance, particularly at the lowest energy input

Table 2-8 Continued.

Paper	AM parameters	Matrix	Source	Concentration	Microstructure	Properties
Tao et al.(Tao, Yao, Zhang, et al., 2018)	Evaluating beam current (pre-sintered)	CP-Ti	B ₄ C particles (avg: 5 µm)	4 wt. %	Low energy input: unreacted B ₄ C with TiB ₂ whiskers, plus TiB and TiC. High energy input: coarse TiB. Rich volume fraction of (TiB + TiC)	Maximum hardness: 7.75GPa Maximum reduced modulus: 150.3GPa Minimum friction coefficient: 0.47 Highest microhardness (634HV) among all TMC coatings tested Maintained hardness at 450°C (480HV)
Yun et al.(Yun et al., 2004)	Constant	Ti6Al4V/Ti	B4C particles (20-50 µm) and Ti particles Flux: CaF ₂	25 wt.% Ti-25 wt.% B ₄ C-50 wt.% CaF ₂		
WAAM: Wang et al.(Z. Wang et al., 2023)	Decreasing current with more deposited layers	Ti6Al4V/Ti	Flux-cored wire; core: B ₄ C, C, Ti6Al4V and Al60V40; shell: Ti	5 wt.% TiB + TiC 10 wt.% TiB + TiC	Middle region: Interlaced TiB and TiC forming a quasi-continuous network with a basket-weave pattern. Top layer: Less continuous TiB and TiC network; predominately martensite. Bottom layers: Microstructure intermediate between middle and top regions.	Microhardness increased by 35.1% compared to Ti substrate. Optimal wear resistance at 5 wt.% with 27.5% less wear loss than non-reinforced parts.

2.6.3 Effect of Boron on Martensitic Phase

Martensitic transformations in titanium and its alloys can be influenced by rapid cooling from the stability range of the β phase (Motyka et al., n.d.). Interestingly, boron is known to impact the formation of these martensitic phases. In casting, boron has been shown to lower the martensitic transformation temperatures in titanium. Specifically, Horiuchi et al. (Horiuchi et al., n.d.) noted that for Ti-24Nb-3Al (mol.%) alloy produced by arc melting, all martensitic transformation temperatures decreased with the addition of boron. Notably, the start temperature for martensitic transformation, known as M_s , dropped linearly with increasing boron content up to 0.05 wt.%. Beyond this point, M_s plateaued, unaffected by further increases in boron content as TiB formation commenced. This suggests that M_s is directly related to the solubility of boron in the alloy, decreasing until it reaches a solubility limit at 0.05 wt.%. Any additional boron beyond this threshold precipitates as TiB, leaving the solute concentration—and consequently M_s —constant. In AM, the influence of boron on martensite can be more complex owing to the extreme cooling rates encouraging the formation of non-equilibrium phases.

Rahman Rashid et al. (Rashid et al., 2018) found that in DEDed Ti6Al4V components, the microstructure initially featured martensitic α' needles, but shifted to fine α -laths with the introduction of just 0.05 wt.%B. Expanding on this, Patil et al. (A. Patil et al., 2019) observed that the addition of TiB₂ progressively transformed martensitic α' -Ti laths into a two-phase structure of equiaxed α and colony α in PBF-LB/M Ti6Al4V parts. Notably, in samples modified by 0.5 wt.% TiB₂, the α' martensite distribution was interrupted, and α' -laths were notably non-existent in areas where TiB whiskers had developed. A similar transition was seen in PBF-LB/M Ti-6Al-7Nb components, where the addition of 1.5 wt.% TiB₂ (equivalent to 0.45 wt.%B) changed the microstructure from α' martensite to a mix of α and α' phases (N. Singh et al., 2021).

The transition from α' martensite to α phases following the addition of boron may be due to several factors. The change can be traced back to the diffusion of boron (or nitrogen from non-elemental boron sources) into the matrix, which alters the martensitic temperatures previously observed in titanium castings (J. Avila et al., n.d.; Horiuchi et al., n.d.). A peritectoid reaction between β -Ti and TiB could lead to the formation of α -titanium rather than martensitic α' (A. Patil et al., 2019). Thermal and kinetic influences also play significant roles. Common boron sources absorb laser energy more efficiently than titanium, raising the peak temperature of the molten pool in laser-based processes (Das, Balla, et al., n.d.). The heat from exothermic reactions involving TiB and potential other intermetallics, combined with the heat-retaining properties of these refractory phases, might slow down the cooling process (J. Avila et al., n.d.; Gordienko & Evtushok, 2001). This deceleration could reduce the nucleation rate, potentially preventing the formation of α' martensite. This effect is particularly relevant in DED-LB, typically exhibiting slower cooling rates compared to PBF-LB/M. Typical cooling rates are around 10^3 – 10^5 °C/s for DED-LB and 10^3 – 10^8 °C/s for PBF-LB/M (Ahn, 2021; M. Bermingham et al., 2020; DebRoy et al., n.d.; J. Otte, Zou, et al., n.d.).

In summary, while sharp temperature gradients and rapid cooling generally encourage the development of martensitic-type microstructures in AM, the introduction of boron can disrupt the formation of α' martensite. This is due to both a variation in the martensitic transformation temperatures and the additional heat introduced into the system.

2.6.4 Grain Refinement

Historical evidence from titanium casting and recent research highlights the effectiveness of even trace amounts of boron in refining the grain size of titanium and its alloys in AM. Major grain refinement in CP-Ti lattice structures produced via PBF-LB/M after adding 0.8 wt.%BN (J. Otte, Soro, et al., n.d.). In another study, it has been demonstrated addition of 1 wt.% of BN significantly reduced the martensite lath width in PBF-LB/M fabricated components, reducing it from 1.4 μm to 300 nm. The introduction of boron and its reaction with titanium lead to various synergistic effects contributing to grain refinement. In the melt pool, primary TiB crystals can serve as heterogeneous nucleation sites for β -Ti(Y. Hu, Cong, et al., n.d.), and even partially unmelted boron particles or other boron-sourcing particles may act as potent nucleating agents (J. Otte, Zou, et al., n.d.). Additionally, the dissociation of boron into the molten metal induces constitutional supercooling. These factors together—nucleants in conjunction with solute—support the refinement of prior β -Ti grains. This is explained by the interdependence theory, suggesting effective nucleation in a melt requires both sufficient solute and nucleation sites; neither alone is adequate to achieve grain refinement (StJohn et al., n.d.).

In AM, similar to titanium casting, the addition of boron results in a shift from globular to branched dendritic grain structures in β -Ti(A. Xue et al., n.d.). This alteration enhances the grain boundary area, which serves as a platform for increased nucleation of the α phase (M. Bermingham, McDonald, Nogita, et al., n.d.). Eutectic TiB nanowhiskers, observed in solidified TMCs, act as effective nucleants for the α phase, which contributes to the reduction of grain size in the final consolidated parts (Y. Yang et al., n.d.). Additionally, the preferential positioning of TiB at the grain boundaries inhibits grain growth during subsequent heat treatments, a process known as Zener pinning (J. Avila et al., n.d.).

Boron is noteworthy in grain refinement for its exceptionally high Q value (M. Bermingham et al., 2008; M. Bermingham, McDonald, Materialia, et al., n.d.). Introducing components into a melt can significantly enhance grain refinement through accelerated heterogeneous nucleation, a combined effect of both nucleant and solute effects (Easton, Materialia, et al., n.d.; Easton & StJohn, 1999). Specifically, Q value of boron promotes rapid constitutional undercooling, leading to quick nucleation ahead of the S/L front and ultimately, smaller grain sizes (Easton, A, et al., n.d.). For comparison, both aluminium and vanadium in titanium exhibit a Q value of zero, indicating no significant impact on grain refinement at any concentration, which is evident in the large columnar prior- β grains of AMed Ti6Al4V parts, despite a 10 wt.% concentration of Al and V (M. Bermingham, Kent, et al., n.d.; K. Zhang et al., n.d.). On the other hand, the growth restriction factor for boron in titanium is significantly higher, estimated at $65C_0$, where C_0 denotes the weight percentage of boron (M. Bermingham et al., 2008; M. Bermingham,

McDonald, Materialia, et al., n.d.). The growth restriction factor is generally proportional to the solute content, but the grain refinement effectiveness of boron in Ti6Al4V parts appears to follow a more complex relationship with its concentration. Xue et al. (A. Xue et al., n.d.) found that while boron consistently enhanced microstructural refinement, the correlation between boron concentration and grain size reduction was not linear. Specifically, increasing the boron content from 0 to 0.08 wt.% had a more pronounced effect on grain size reduction than raising it from 0.08 to 0.25 wt.%. This aligns with findings in other studies suggesting a saturation point in grain refinement effectiveness around 0.10 wt.% of B in titanium alloys (Sen et al., n.d.; Tamirisakandala, Bhat, Tiley, et al., n.d.; Y. Yang et al., n.d.). In contrast, Zhang et al. (K. Zhang et al., n.d.) observed continual decrease in β grain size in similar parts even with boron levels up to 1 wt.%, attributing this variance to differences in cooling rates. They explain that higher cooling rates compress the solute (B) diffusion layer at the S/L interface, leading to maximum constitutional undercooling occurring nearer to the interface and thus, promoting more nucleation incidents. This could imply a higher solute saturation point under faster cooling conditions. However, at extremely high cooling rates, the constitutionally undercooled region might disappear, potentially preventing nucleation ahead of the solidus/liquidus interface (K. Zhang et al., n.d.).

The effectiveness of boron as a grain refiner has also been studied in β -type alloys, such as TiAl, where grain refinement can be toggled on or off depending on whether boron is added above a certain critical threshold, typically around 0.5 at.%. However, the precise amount of boron needed varies depending on the presence of other ternary or quaternary alloying elements. Furthermore, the presence of strong boride-forming elements like tantalum and niobium can raise the minimum boron concentration required for effective grain refinement (Intermetallics & 2000, n.d.). Despite these challenges, Huang et al. (D. Huang et al., n.d.) have found that introducing boron via 0.5 wt.% of LaB₆ offers a viable method to mitigate the inherent brittleness of TiAl alloys in AM. They noted that the grain size decreases as boron concentration increases, which in turn lessens the brittleness of the alloy. However, exceeding 0.5 wt.% LaB₆ leads to the agglomeration of precipitates, decreasing the density and mechanical properties of the parts, such as yield strength, ultimate strength, and compression deformation. Similarly, Batalha et al. (Batalha et al., 2022) observed significant microstructural changes in a Ti-35Nb-7Zr-5Ta (TNZT) β -type alloy after adding 1 wt.% of TiB₂ through PBF-LB/M processing. Initially, the unmodified TNZT alloy had large, elongated β grains spanning multiple layers. The addition of TiB₂ nearly halted this epitaxial growth, transforming the structure to columnar-dendritic crystals. This modification significantly reduced the average grain size in the TNZT alloy from 327 μm to 58 μm in the longitudinal direction and from 72 μm to 49 μm in the transverse direction.

In summary, adding just a small amount of boron can significantly enhance grain refinement in AM titanium and its alloys. This effect is largely due to the potent solute impact of boron. The effectiveness of boron in refining grains is also influenced by the printing conditions, particularly the cooling rate. Higher cooling rates can raise the solute saturation point,

enhancing grain refinement unless the constitutionally supercooled zone at the S/L interface is eliminated.

2.6.5 Columnar-to-Equiaxed Transition

In metal AM, heat primarily dissipates along the build direction, causing solidification to start from previously deposited layers and progress upwards. Without heterogeneous nucleation sites, the microstructure of metals, including titanium and its alloys, often shows epitaxial growth (M. Bermingham, StJohn, et al., n.d.). This pattern is particularly prevalent in titanium alloys, where columnar prior- β grains can extend vertically through multiple layers, growing several millimetres in length and hundreds of microns in width (Chao et al., n.d.). These coarse columnar grains lead to anisotropy in mechanical properties, reducing ductility and lowering low-cycle fatigue resistance in titanium alloys (M. Bermingham, StJohn, et al., n.d.; A. Xue et al., n.d.).

Small amounts of boron can significantly affect the CTE transition in AM, though the impact varies with the specific AM technique used. For example, Wang et al. (L. Wang et al., 2023) found addition of 0.5 wt.% BN particles to Ti6Al4V in PBF-LB/M resulted in a structure with alternating bands of columnar and equiaxed prior- β grains. In contrast, increasing boron concentration from 0.08 to 0.17 wt.% almost halted the epitaxial growth of prior- β grains in Ti6Al4V in DED-LB (A. Xue et al., n.d.). In PBF-EB, Mahbooba et al. (Mahbooba et al., 2017) found that increasing boron content from 0.25 to 0.50 wt.% gradually narrowed the width of columnar prior- β grains but did not change their columnar morphology due to dominant unidirectional heat transfer and repeated layer melting characteristic of PBF-EB. Furthermore, at 1 wt.%B, prior- β grain boundaries became indistinguishable in optical images, similar to findings by Zhang et al. (K. Zhang et al., n.d.) that high boron levels can obscure α_{GB} , making it difficult to identify prior- β grains through optical microscopy.

Boron concentration significantly influences microstructural evolution in AM, especially in strongly hypoeutectic systems where proeutectoid TiB particles cannot form, leaving only partially unmelted boron or other boron-sourcing particles as available nucleants. Although boron is an effective grain refiner, its impact may be limited by the lack of sufficient nucleants, potentially hindering the CTE transition in prior- β grains (M. Bermingham, Kent, et al., n.d.). Thus, it is critical to optimize both boron concentration and printing parameters, as the final microstructure is determined by the interaction between material composition and processing conditions. Different AM techniques or changes in processing parameters, even with the same chemical composition, can result in varied microstructural textures. For example, the creation of deep melt pools in high-power DED or PBF-LB/M can disrupt epitaxial growth regardless of boron levels. Adjusting Marangoni convection by changing energy density and switching to keyhole mode can significantly refine grains compared to conduction mode (D. Zhang et al., 2020).

The morphology of the α phase in AM is significantly influenced by the characteristics of prior- β grains, as α phase typically nucleates and grows from the vicinity of prior β -Ti grain boundaries (M. Bermingham, McDonald, Nogita, et al., n.d.). The addition of boron modifies these prior- β grains, leading to smaller and more equiaxed α phases at room temperature (Sen et al., n.d.; A. Xue et al., n.d.). In some cases, α grains may nucleate on TiB whiskers rather than from prior- β grain boundaries, further randomizing the structure (K. Zhang et al., n.d.). This effect was clearly shown in parts produced by DED-LB by Chao et al. (Chao et al., n.d.), where the addition of 0.1 and 0.4 wt.% BN nanotubes resulted in prior β -Ti grains that were uniformly small and equiaxed, averaging 33 μm and 9 μm in size respectively. This fine grain size restricted α -lath growth, significantly reducing their aspect ratio to about 2.1, compared to over 10 in untreated Ti6Al4V parts. Zhang et al. (K. Zhang et al., n.d.) also noted that adding boron to Ti6Al4V processed by DED-LB decreased the size of prior- β grains, with thickness reduced from over 400 μm in untreated samples to less than 90 μm after adding 1 wt.% B, and these grains no longer elongated along the build direction. This addition also diminished the texture intensities of the α phase and reduced the average α lath thickness from 1.23 μm to 0.59 μm while eliminating α_{GB} (K. Zhang et al., n.d.). In Ti6Al4V parts fabricated by WAAM, the addition of 1.3 wt.% boron did not significantly alter the width of α -laths but reduced their length by more than fourfold, resulting in a more equiaxed shape and reduced aspect ratio (M. Bermingham, Kent, et al., n.d.). Huo et al. (Huo et al., 2023) reported similar findings in high-Nb TiAl alloys processed by DED-LB. The presence of niobium along with rapid cooling eliminated the B2 (β) phase at room temperature. Adding just 0.5 at.%B initiated the formation of primary TiB whiskers with a random orientation, which hindered the growth of large prior- β crystals and led to the formation of a finer α phase at room temperature. As a result, the microstructure featured very fine lamellar colonies composed of alternating α_2 and γ lamellae. The average size of these lamellar colony grains decreased from 75 μm (without B) to 45 μm (with 0.5 at.%B). Although not achieving a complete CTE transition, there was a notable reduction in the phase transformation texture, an indicator of lamellar orientation, from 58 to 20 (Huo et al., 2023). While boron addition often leads to more equiaxed grains, it does not necessarily reduce anisotropic effects in the material. For instance, Bermingham et al. (M. Bermingham, ..., et al., n.d.) studied the anisotropic behaviour of Ti6Al4V parts made via WAAM with trace amounts of LaB₆ added. They found that although boron decreased the α -Ti grain size and effectively removed grain boundary α , the anisotropy in the parts actually increased. This was due to the formation of large (over 50 μm), highly textured TiB needles, which influenced the directional response of material to tensile stress and became sites for crack initiation.

In summary, boron facilitates the columnar-to-equiaxed transition of prior- β grains, often resulting in the development of refined and more equiaxed α grains. However, the morphology of prior- β grains may still exhibit a columnar structure in AM processes like PBF-EB, where the strong unidirectional heat transfer and repeated layer melting dominate over the randomizing effects induced by boron. The effectiveness of triggering the columnar-to-equiaxed transition is highly dependent on the interplay between boron concentration and

processing parameters. In hypereutectic systems, primary TiB crystals can serve as nucleation sites that disrupt the texture of the β phase. Conversely, high-power DED and PBF-LB/M can create deep melt pools that tend to inhibit epitaxial growth.

2.6.6 Densification

In the context of additive manufacturing of boron-modified titanium alloys achieving fully dense parts relies heavily on precise adjustment of process parameters. Typically, metallic systems containing intermetallic compounds such as TiB (melting point 2200°C (Das, Balla, et al., n.d.)) or TiB₂ (melting point 3225°C (Attar et al., n.d.)) pose significant processing challenges due to their higher melting points compared to CP-Ti (melting point ~1670°C (Cezairliyan & Miller, 1977)) and its alloys (e.g., Ti6Al4V, melting point range 1604°C to 1670°C (Keaveney et al., 2020)). Furthermore, the addition of solid-state reinforcement within the melt pool alters the dynamic viscosity of the metal matrix (Attar et al., n.d.). In PBF, optimizing processing parameters is particularly difficult for highly porous lattice structures. This is because numerous overhanging features require printing without supports, downskin surfaces need optimization to minimize adhesion of unmelted particles, and the layer perimeter is more significant than the interior due to the thin struts (J. Otte, Soro, et al., n.d.).

Otte et al. (J. Otte, Zou, et al., n.d.) examined the influence of various combinations of laser power and hatch distance on the densification of CP-Ti powders pre-mixed and coated with 2.5 vol% ($\approx$ 1 wt.%) of nanosized BN platelets. They observed that reducing the hatch distance generally enhanced densification at all laser power levels. When the hatch distance was less than 0.1mm, the relative density of the printed parts consistently exceeded 99%, making the impact of laser power negligible. Nevertheless, laser power significantly affected the dissolution of BN in the melt and subsequent reactions with titanium. Otte et al. (J. Otte, Zou, et al., n.d.) suggested that incorporating BN, particularly in its nanoscale form, could facilitate densification. Nano-BN can occupy spaces between larger titanium particles in the powder bed, enhancing bed density and potentially leading to denser final parts. Additionally, laser absorption coefficient of BN surpasses that of titanium (Das, Balla, et al., n.d.), and its high thermal conductivity, measured at 585 W/(mK) for hexagonal BN (J. Otte, Zou, et al., n.d.), aids in efficient heat transfer. When situated between titanium or its alloy particles, BN can enhance laser beam interaction and lateral heat distribution (J. Otte, Zou, et al., n.d.). Furthermore, the exothermic nature of reactions between titanium and boron (Gordienko & Evtushok, 2001) introduces extra heat (J. Otte, Zou, et al., n.d.) and promotes increased mixing within the melt pool (R. Banerjee et al., 2004).

Similar considerations apply to other boron sources with higher laser absorption coefficients than titanium. However, the formation of thermally stable intermetallics and the presence of coarse reaction products like primary (hypereutectic) TiB are likely to disrupt the melt pool flow and its lateral spreading, potentially causing microstructural defects and reducing the density of printed parts (Essien & Vaudreuil, 2022). He et al. (Y. He et al., 2019) also demonstrated in powder-free single-track experiments that the melt pool geometry in PBF-

LB/M changes with increasing boron content. Adding 1 and 2 wt.% B to Ti6Al4V caused significant melt pool geometry changes only in the low-power range. However, with 5 and 10 wt.% B addition, these changes extended to higher power regions. At high boron concentrations, normal melt pool geometries were only observed within a narrower processing window than for neat Ti6Al4V. This suggests that achieving defect-free parts would be more challenging for Ti6Al4V with high boron content, or at least process parameter flexibility would be reduced.

Although various studies report the absence of notable cracks in boron-modified components (Attar, Bönisch, Calin, Zhang, Zhuravleva, et al., 2014; Cai et al., n.d.; Das, Balla, et al., n.d.; Das, Bhattacharya, et al., n.d.; Y. Hu, Ning, et al., n.d.; F. Wang et al., 2008), achieving defect-free parts necessitates the simultaneous optimization of boron content and process parameters. For instance, Han et al. (C. Han et al., 2020) conducted a preliminary test identifying 167 J/m as the optimal linear energy density for fabricating TMCs via LB-PBF. They found that defect-free components were achieved with a 1 wt.%B₄C content, whereas specimens with 2 and 3 wt.%B₄C exhibited micropores. Furthermore, TMCs with 5 wt.%B₄C developed macro-cracks, leading to a significant decrease in relative density and structural integrity, preventing the production of tensile test specimens (C. Han et al., 2020). Similarly, He et al. (D. He et al., 2023) observed that the addition of LaB₆ increased the laser absorption of Ti6Al4V, facilitating printing. However, excessive LaB₆ caused metallurgical pores due to unfilled voids left by evaporating Al, owing to impaired Marangoni convection. Additionally, high filler content led to LaB₆ particle aggregation, serving as crack initiation sites. He et al.(D. He et al., 2023a) identified 3 wt.% as the optimal concentration to be added, balancing laser absorption and melt flow, and required a high linear energy density (305.56 J/mm) to fully melt LaB₆ particles and prevent defects. The formation of cracks during printing is significantly influenced by the characteristics of the metal matrix, a factor often overlooked in the literature. Specifically, titanium and its alloy components are prone to cracking when ceramic particles are incorporated. However, Huang et al. (D. Huang et al., n.d.) demonstrated that adding 0.5-1 wt.% LaB₆ could mitigate the brittleness of a β -solidifying TiAl alloy. This addition transformed the coarse, nearly lamellar microstructure of the original TiAl alloy into a duplex microstructure with fine equiaxed grains, which more effectively accommodated strain (D. Huang et al., n.d.).

For certain metal-additive combinations, merely optimizing process parameters is insufficient; additional techniques like pre-heating the substrate (Huo et al., 2023) or localized heating after each layer deposition (Z. Wang et al., 2023) are required to prevent cracking. Su et al. (Su et al., 2020) explored the challenges of additive manufacturing in TiB-reinforced titanium matrix through a feasibility study. They assessed the printability of Ti6Al4V with 1% and 3% TiB₂ using PBF-LB/M, decreasing scan speeds from 1200 mm/s to 300 mm/s. This adjustment increased the volumetric energy density from 104.17 J/mm³ to 416.67 J/mm³. Crack-free Ti6Al4V was achievable at 125 J/mm³. However, for composites with 1% TiB₂, 250 J/mm³ was necessary, and for 3% TiB₂, 416.67 J/mm³ was required. Notably, higher energy density increased the relative density of composite parts, while density of Ti6Al4V decreased likely

due to aluminium evaporation causing keyhole defects (Su et al., 2020). Similarly, Kang et al. (N. Kang et al., 2016) found that titanium parts with 2% CrB₂ processed by PBF-LB/M had reduced density (97.5% to 93.5%) as scan speed dropped from 1250 mm/s to 1000 mm/s, attributed to balling and dross formation at lower speeds, which compromised surface quality and powder layer distribution.

Hu et al. (Y. Hu, Ning, et al., n.d.) observed that introducing 1.6 wt.%B led to the appearance of large clusters of spherical particles on the surface of DED-LB titanium components. Additionally, internal pores were linked to this 'balling' phenomenon, attributed to the poor wettability of the newly formed TiB particles. With other printing parameters constant, an increase in laser power enhanced the quality of printed parts, reducing lack-of-fusion defects and micropores. However, despite the similar thermodynamic behaviour of TiB and titanium, increasing laser power (and thereby energy density) could also elevate residual stresses in the printed parts (Y. Hu, Ning, et al., n.d.). The elevated laser absorption coefficient of LaB₆ particles is expected to enhance the formation of a larger and deeper melt pool (D. He et al., 2023). However, He et al. (D. He et al., 2023) found that the density of Ti6Al4V components produced by PBF-LB/M decreased with LaB₆ addition, due to an increased fraction of pores trapped in the melt pool from the high cooling rate. In addition to the trapped gas bubbles, altered Marangoni convection and additional wettability issues likely contributed to the increased porosity with higher LaB₆ content. Conversely, no pores or defects were observed at the interface between α grains and the TiB and La₂O₃ precipitates.

Residual porosity and unreacted primary particles are notably prevalent in B₄C-modified titanium alloys, attributed to high melting point and low thermal diffusivity of B₄C. Enhancing beam energy may facilitate the dissolution of B₄C particles and promote densification in AM-LB; however, this may also lead to the formation of coarse precipitates that detract from the hardness and strength of the printed components (Fereiduni et al., 2019; Tao, Yao, Zhang, et al., 2018; Xia et al., 2017; Yi et al., n.d.). Xia et al. (Xia et al., 2017) demonstrated that reducing the scan speed similarly increases energy density in the melt pool, mirroring the effects of higher beam energy. The characteristics of pores in printed parts change with scan speed adjustments. At a low scan speed (600 mm/s, relative density of 98.9%), small spherical pores predominantly result from gas bubbles entrapped within the melt pool. With increased scan speed (1000 mm/s, density of 96.8%), pores become larger and more elongated due to reduced thermal convection. At 1400 mm/s (density of 93.5%), large irregular pores and lack-of-fusion defects become more common. At 1800 mm/s (density of 89.2%), these defects worsen, and increased melt viscosity hinders proper melt pool spreading. Despite the potential negative effects of high laser power and low scanning speed, the size of B₄C powders is crucial; smaller B₄C particles have a higher likelihood of complete dissolution under consistent printing parameters.

In summary, boron compounds typically exhibit higher laser absorption coefficients compared to titanium and its alloys. When boron-source powders, of nano- or sub-micron scale, adhere to

the metal particle surfaces, the resulting surface roughness decreases laser reflection, potentially enhancing printing efficiency in AM-LB processes. Moreover, the exothermic nature of the reactions between boron-source particles and titanium promotes better mixing within the melt pool. However, the inclusion of refractory ceramic particles tends to cause porosity and cracking due to the interference with Marangoni convection. To produce defect-free components, it is crucial to optimize both the material system composition, particularly the filler concentration, and the printing parameters concurrently.

2.6.7 Mechanical Properties

A thorough comprehension of processing-structure-properties-performance relationships is vital for the broader application of metal AM in industry, particularly in fatigue and fracture-sensitive applications. This concept emphasizes the processing conditions, such as the appropriate combination of printing parameters and feedstock, determine the microstructure of the resulting material. Consequently, the structure of material influences its mechanical properties, which in turn dictate the performance of the AMed component (Hrabe et al., 2016). To address this necessity, Table 2-4 to Table 2-8 in Section 2.5.1 (elemental boron) and Section 2.5.2 (other boron-sources) compile data on the AM method, feedstock materials (including metal matrix, filler type, and loading), resultant structure, and related mechanical properties. This information may facilitate the design of new components with optimized properties for specific applications. Where feasible, the mechanical properties of the base metal matrix are provided for comparison. A key observation from Table 2-4 to Table 2-8 is that the addition of boron generally enhances material strength. For instance, depth-sensing nanoindentation tests showed that incorporating 0.4 wt.%BN nanotubes achieved a yield strength of approximately 1407 MPa and an ultimate strength of around 1678 MPa, representing a significant increase of 50% and 40%, respectively, compared to Ti6Al4V produced by DED-LB (Chao et al., n.d.). Similarly, Otte et al. (J. Otte, Zou, et al., n.d.) reported that TMCs with 2 wt.%BN nanoplatelets exhibited a maximum increase in Young's modulus by 26.5%, yield strength by 79.2%, and ultimate tensile strength by 57.8% over CP-Ti parts produced by PBF-LB/M, as measured by tensile testing at room temperature.

According to Zhou et al. (Z. Zhou et al., 2021), the primary mechanisms behind the strength enhancement are (i) Hall-Petch (boundary) strengthening and (ii) load-bearing transformation (load-sharing or shear-lag) strengthening. The grain size in metals restricts the effective slip length of dislocations; smaller grains result in shorter dislocation slip lengths (Sen et al., n.d.). Boundary strengthening involves microstructural refinement, reducing the distance for dislocation motion. This increases the yield strength, which can be estimated using the Hall-Petch model as follows:

$$\Delta\sigma_{HP} = K \left(\frac{1}{\sqrt{d_2}} - \frac{1}{\sqrt{d_1}} \right) \quad 2.13$$

where K denotes the Hall-Petch constant, while d_1 and d_2 represent the mean grain sizes pre- and post-refinement, respectively (Z. Zhou et al., 2021). The increase in yield strength resulting from load-bearing transformation (LBT) can be quantified as follows:

$$\Delta\sigma_{LBT} = 0.5\sigma_{0.2m}V_R\left(\frac{l}{d}\right)_R\omega_0 \quad 2.14$$

where yield strength of the metal matrix is represented by $\sigma_{0.2m}$, while V_R , $(l/d)_R$, and ω_0 denote the volume fraction, aspect ratio, and orientation factor of the reinforcement, respectively. For randomly oriented nanowhiskers, ω_0 equals 0.27 (Z. Zhou et al., 2021).

In TiB-reinforced titanium alloys, the Hall-Petch effect, due to reduced grain size, enhances yield strength at room temperature. Additionally, fine needle-like TiB phases on grain boundaries impede dislocation motion on the slip plane, further increasing yield strength during plastic deformation (Y. Hu, Ning, et al., n.d.; A. Xue et al., n.d.). Despite its frequent omission in literature, Hu et al. (Y. Hu, Cong, et al., n.d.) suggested that dislocation hardening also contributes to increased yield strength as follows:

$$\Delta\sigma_{dis} = \sqrt{(\Delta\sigma_{Or})^2 + (\Delta\sigma_{th})^2 + (\Delta\sigma_{geo})^2} \quad 2.15$$

where $\Delta\sigma_{Or}$ represents the Orowan stress required for a dislocation to navigate through an array of TiB whiskers. $\Delta\sigma_{th}$ denotes the stress increase due to the thermal expansion mismatch between TiB and titanium (or its alloys), which is negligible. $\Delta\sigma_{geo}$ signifies the stress increase from strain gradient effects related to the dislocation geometry distribution.

The extent to which each strengthening mechanism contributes is predominantly influenced by the volume fraction of TiB, which is primarily determined by the boron concentration (Sen et al., n.d.). Dong et al. (Dong et al., 2020) indicate that increasing the boron concentration typically enhances the LBT (shear-lag) effect and HP (fine-grain) effect, while diminishing the Orowan effect, thereby reducing the contribution from dislocation hardening. Nevertheless, irrespective of the relative contributions of individual mechanisms, the model by Li et al. (Q. Li et al., 2009) suggests that the total yield strength of a metal matrix composite arises from the cumulative effect of various strengthening mechanisms, expressed as:

$$\sigma_{ys} = \sigma_{0.2m} + \Delta\sigma_{HP} + \Delta\sigma_{LBT} + \Delta\sigma_{dis} \quad 2.16$$

In addition to yield strength, the Vickers hardness of titanium and its alloys increases with boron addition. For instance, the hardness of DED-LB parts increases from approximately 342HV for Ti6Al4V to about 400HV with 0.1 wt.%BN nanotubes, and up to around 433 HV with 0.4 wt.%BN nanotubes added counterparts (Chao et al., n.d.). Rahman Rashid et al. (Rahman

Rashid et al., 2018) similarly reported an increase in hardness of DED-LB parts from 390-450HV to 510-600HV when Ti6Al4V was modified with 0.05 wt.%B, where the hardness gradient is associated with an increase from the bottom to the top of the track. Furthermore, the Vickers hardness of CP-Ti parts produced by DED-LB rises from 304HV to 393HV with 1.6 wt.%B addition (Y. Hu, Zhao, et al., n.d.). This hardness enhancement is attributed to the increase in yield strength due to boron addition, which improves resistance to plastic deformation (J. Avila et al., n.d.; Y. Hu, Ning, et al., n.d.). Additionally, TiB and other intermetallics, if present, are significantly harder than the surrounding titanium matrix (R. Banerjee et al., 2004a), which explains why both hardness and yield strength of boron-modified titanium increase with boron content, though hardness increases more rapidly than yield strength (Sen et al., n.d.). BN as a boron source introduces nitrogen solute atoms in the solidified titanium matrix, stabilizing the α -phase and significantly enhancing solid solution hardening (Chao et al., n.d.). Similarly, the increased hardness of B₄C-modified parts is partly due to the dissolution of carbon in the titanium matrix, which is more soluble than boron (Tao, Yao, Zhang, et al., 2018). The enhanced hardness of boron-modified titanium and its alloys generally leads to increased wear resistance (A. Patil et al., n.d.; Su et al., 2020; F. Wang et al., 2008), unless unreacted particles, which are harder than the matrix but easily detached due to weak bonding, are present (Xia et al., 2017). Optimal wear resistance is achieved with fine, homogeneously distributed eutectic TiB whiskers, as opposed to coarse primary TiB precipitates in strongly hypereutectic microstructures (Galvan et al., 2004). Bermingham et al. (M. Bermingham, Kent, et al., n.d.) observed extensive twinning in Ti6Al4V parts deposited by WAAM under compressive load, where twin transmission along coarse α colonies induced stress drops and audible acoustic phenomena in the plastic flow region. Adding 1.3 wt.%B mitigated, but did not suppress, twinning by preventing the formation of large α colonies responsible for extensive twinning transmission, with borides at grain boundaries potentially limiting twin growth. Nevertheless, the incorporation of TiB can detrimentally affect the ductility of titanium (Chao et al., n.d.; Y. Hu, Zhao, et al., n.d.; J. A. Otte et al., 2020). Zhang et al. (K. Zhang et al., n.d.) reported that Ti6Al4V components fabricated via DED-LB exhibited a ductile failure mode at a boron concentration of 0.05 wt.% but transitioned to a brittle mode when the boron concentration increased to 0.5 wt.%. This is attributed to the inherent brittleness of TiB, which exacerbates as the connectivity of TiB precipitates intensifies (M. Bermingham, Kent, et al., 2015.; Chandran & Panda, 2002). The utilization of BN as a boron precursor also presents challenges. The α -phase ductility, particularly in unalloyed titanium, is highly susceptible to interstitials, notably nitrogen (Chandran & Panda, 2002). TiN, which is similarly brittle, can form large dendrites that propagate transgranular cracks (Das, Bhattacharya, et al., n.d.). This reduction in ductility is particularly problematic in lattice structures and scaffolds, where the thin walls are incapable of accommodating rigid and brittle TiB particles (Attar et al., 2015).

Certain studies indicate that the addition of boron does not invariably induce embrittlement. For instance, the previously mentioned susceptibility to cracking in a brittle β -solidifying TiAl alloy was mitigated by adding an appropriate amount of LaB₆ (approximately 0.5 wt.%) and

optimizing the DED-LD parameters, resulting in a fine-grained duplex microstructure (D. Huang et al., n.d.). Nonetheless, the reduction in ductility often linked to the growth of brittle intermetallics and the presence of interstitials remains a concern. The structural refinement of reinforcements, such as TiB and other intermetallics, is essential for addressing this issue (Chao et al., n.d.; Huo et al., 2023; J. A. Otte et al., 2020). Smaller particles increase the specific interfacial area for bonding with the matrix, enhancing the strengthening effect at low filler loadings. Conversely, larger particles can act as inclusions, causing stress concentration and premature failure at low strain. AM generally results in significantly smaller TiB precipitates compared to conventional manufacturing due to faster cooling rates (Attar, Bönisch, Calin, Zhang, Zhuravleva, et al., 2014; R. Banerjee et al., 2004; Rashid et al., n.d.). However, the size of TiB and other precipitates is significantly influenced by the interaction between printing conditions and additive content. According to solidification theory, the average size of the solidification microstructure is inversely related to the square root of the cooling rate. Therefore, finer microstructural features are promoted by printing with low energy input and high scan speed, as this combination enhances thermal gradients near the melt zone, resulting in higher cooling rates (Das, Balla, et al., n.d.; Das, Bhattacharya, et al., n.d.). Conversely, increasing boron concentration elevates the peak melt pool temperature due to higher laser absorptivity of boron compared to titanium and the exothermic reactions between boron and titanium. This elevation leads to the formation of coarser reaction products (Das, Balla, et al., n.d.; Das, Bhattacharya, et al., n.d.). The growth rate, k , is known to depend on the absolute operating temperature, T , as per (Xia et al., 2017):

$$k = k_0 \exp\left(-\frac{Q_k}{2RT}\right) \quad 2.17$$

where R represents the gas constant, while k_0 and Q_k correspond to the frequency factor (17.07×10^{-4}) m/s^{1/2} and activation energy (190.3 kJ/mol) for TiB, respectively (Fan et al., n.d.). Considering the one-dimensional growth of TiB, the whisker length, x , varies with time, t , as described in (Xia et al., 2017):

$$x = k\sqrt{t} \quad 2.18$$

While the kinetics in most AM methods may significantly deviate from equilibrium due to high cooling rates, a rise in local temperature is still anticipated to accelerate the growth of larger precipitates. The reinforcement shape is also crucial; needle-like and fiber-like reinforcements with high aspect ratios result in enhanced strengthening effects (J. A. Otte et al., 2020; Tjong & Mai, 2008). Ductility may be partially restored by increasing the β phase fraction through the addition of β -stabilizers such as niobium (Chandran & Panda, 2002). However, as discussed by Chandran and Panda (Chandran & Panda, 2002), previous experience with traditional manufacturing techniques, such as powder metallurgy and sintering, indicates that the aspect ratio of TiB whiskers, and thus their reinforcing effect, is significantly influenced by the type

and quantity of β stabilizers added to the titanium alloys. An additional potential disadvantage is that boron-induced grain refinement might lower the fracture toughness of titanium. For instance, Sen et al. (Sen et al., n.d.) demonstrated that the toughness of Ti6Al4V castings decreased from 126 to 38 MPa $\times$ m^{1/2} following the incorporation of 0.4 wt.%B. This reduction in toughness was linked to the finer grain size of the boron-modified alloy, which reduced the tortuosity of the crack path based on the fracture surface morphology. Similarly, Zhang et al. (K. Zhang et al., 2023) documented that the crack propagation rate of Ti6Al4V components produced by DED-LB increased with the addition of only 0.05 wt.%B. Despite minimal formation of TiB precipitates, the composites preserved the original ductility of Ti6Al4V. The refined microstructure and more equiaxed texture notably enhanced the high-cycle fatigue resistance of the composites. Zhang et al. (K. Zhang et al., 2023) concluded that, although the fatigue crack initiation resistance of Ti6Al4V was enhanced by boron addition due to reduced effective slip length, the crack growth resistance was diminished, attributed to the smoother (less tortuous) crack propagation along the refined prior- β grain boundaries. TiB particles may also have played a role in the formation of microcracks (K. Zhang et al., 2023).

Ultimately, the addition of boron is typically linked with increased strength and hardness. However, the growth of intermetallic particles may diminish the ductility of titanium alloys. The embrittlement can be alleviated if the TiB needles are nanosized and highly elongated. Regarding fatigue behaviour, boron-induced grain refinement enhances crack initiation resistance but lowers crack growth resistance.

2.7 Knowledge Gaps from Literature

The Ti6Al4V-xB system was selected for this research largely because Ti6Al4V is already a widely used PBF-LB/M material, and existing work shows that introducing boron can offer notable benefits, similar to what has been seen in conventional Ti6Al4V-xB alloys. Boron-modified titanium alloys hold particular promise in aerospace and naval applications, thanks to how they fuse the low weight and strong toughness of a titanium matrix with the excellent strength and rigidity imparted by TiB ceramic precipitates (Boehlert et al., 2009; Gofrey et al., 2000; Tjong & Mai, 2008). Unlike other ceramic reinforcements such as TiC, SiC, or TiB₂, TiB stands out for several reasons (Cai et al., 2017; Morsi & Patel, 2007; Tamirisakandala, Bhat, Miracle, et al., n.d.; Tamirisakandala & Miracle, 2010). First, it offers markedly higher strength and modulus than titanium but with a comparable density, which means these alloys can gain significant rigidity and strength without any additional weight. Second, TiB precipitates exhibit outstanding chemical and thermal stability within a titanium matrix, even at high temperatures, preserving their reinforcing effects. Third, because thermal expansion coefficient of TiB is similar to that of titanium, issues related to thermal stress at the TiB-Ti interface are reduced. Fourth, TiB precipitates can substantially refine prior β -Ti and α -Ti grains (Hill et al., 2005), potentially because they act as pinning agents that inhibit grain growth. Altogether, these advantages greatly enhance the properties of titanium alloys containing boron compared to those without it, which includes improvements in wear resistance, fatigue resistance, and high-

temperature performance (Cai et al., 2017; Ferri et al., 2011; Morsi & Patel, 2007; Tamirisakandala et al., 2005).

Boron additions to titanium alloys, especially when the boron content is high enough to surpass the eutectic threshold, often lead to the development of large primary TiB precipitates in the titanium matrix. These coarse particles can significantly compromise ductility and fracture toughness, as they tend to initiate cracks prematurely (Boehlert et al., 2009). Consequently, managing the size of TiB precipitates is vital for achieving an optimal balance between strength and ductility in boron-containing titanium alloys. Apart from precipitate size, factors such as the shape and spatial distribution of TiB, along with microstructural features in the titanium matrix (e.g., prior β grain size and morphology), also have a major impact on improving the properties of TiB-TMC (titanium matrix composite) (R. Banerjee et al., 2004; Boehlert et al., 2009; Tjong & Mai, 2008). Wang et al. used a complex reactive hot pressing (RHP) method to design a novel TiB network structure in a Ti6Al4V composite (S. Wang et al., 2017). This approach not only enhanced creep resistance but also improved ductility compared to specimens with evenly dispersed TiB whiskers. A similar TiB network layout that offered better performance was seen by Fan et al. in TiB-Ti composites produced via melt spinning (Fan, 1993). However, manufacturing routes like RHP and melt spinning generally involve multiple intricate steps, high energy consumption, and burdensome secondary forming processes, all of which drive up the cost of TiB-TMCs. Laser-based additive manufacturing has emerged as a promising route to address both the formation of coarse TiB precipitates at elevated boron levels and the challenges of more conventional fabrication techniques. Banerjee et al. studied Ti6Al4V-2B (wt.%) samples fabricated by laser-engineered net shaping (LENS) alongside those made by standard arc melting (R. Banerjee, Collins, et al., 2003; R. Banerjee et al., 2004). They discovered that primary TiB particles measured roughly 100 μm in arc-melted specimens, whereas the laser-deposited ones were only about 2.5 μm in size. Further, the distinctive TiB network structure outlined by Wang et al. and Fan et al. was successfully reproduced in Ti1.6B (wt.%) material via LENS, resulting in a notable increase in yield strength compared with the TiB whisker-type microstructure (Fan, 1993; Y. Hu, Cong, et al., n.d.; S. Wang et al., 2017). The PBF-LB/M technique appears highly promising for manufacturing boron-added titanium alloys, primarily due to its rapid solidification feature, which can significantly refine the TiB precipitate size—a refinement not feasible through conventional manufacturing methods. Despite this potential, research on PBF-LB/M-produced TiB-titanium matrix composites (TiB-TMCs) remains limited in number (Attar, Bönisch, Calin, Zhang, Scudino, et al., 2014; N. Kang et al., 2016; Shishkovsky et al., 2017). To date, only a narrow range of TiB-TMC compositions has been explored (approximately 5% to 7% TiB by volume), and within each studied composition, the scope of additive manufacturing process parameters tested remains quite restricted. In existing studies, PBF-LB/M-based TMC production has been achieved by mixing pure Ti powder with ceramic addit(Kühnle & Partes, 2012)ang et al., 2016), B₄C (Kühnle & Partes, 2012), and TiB₂ (Attar et al., n.d.; Y. Chen et al., 2017). These experiments demonstrated considerable grain refinement and notable improvements in material properties—including enhanced yield strength, wear resistance, and corrosion resistance—compared to

commercially pure titanium fabricated by PBF-LB/M. Additionally, boron-modified Ti6Al4V alloys containing 0.1 to 0.25 wt.%B have been investigated via wire-feed laser directed energy deposition (L-DED), yielding refined prior- β grains and improved mechanical properties (M. J. Bermingham et al., 2015; A. Xue et al., 2019). Nevertheless, given the extensive yet scarcely studied parameter ranges for PBF-LB/M processes and TiB-TMC compositions, current knowledge remains insufficient to fully grasp the microstructure optimization potential of LPBF processing for boron-enhanced titanium alloys.

Despite extensive research into PBF-LB/M processing of Ti6Al4V alloys, several significant knowledge gaps persist, particularly regarding the integration of boron to enhance microstructural refinement and mechanical performance. Firstly, while boron is recognized for its potent grain-refining effects, the specific influence of nanosized boron additives on melt pool dynamics, solidification behaviour, and resultant microstructures in PBF-LB/M-produced Ti6Al4V-xB alloys remains underexplored. Most existing literature primarily investigates micro-scale boron additions, leaving critical questions unanswered concerning the effects at the nanoscale. Secondly, achieving fully refined equiaxed microstructures in boron-modified Ti6Al4V alloys via PBF-LB/M has historically proven challenging, and the underlying mechanisms facilitating this microstructural transition, particularly at elevated boron concentrations, remain inadequately documented. Thirdly, the literature lacks comprehensive analytical models integrating PBF-LB/M processing parameters and boron content to predict solidification behaviour and microstructural outcomes. Additionally, the reliance on commercially available pre-alloyed Ti6Al4V-xB powders significantly restricts the systematic exploration of a broad compositional spectrum. Another critical limitation in existing methods is the absence of reliable processes to produce homogeneous satellite powder mixtures for PBF-LB/M.

To bridge these gaps, this study introduces a novel powder-free methodology enabling the in-situ formation of TiB reinforcements during PBF-LB/M processing. This innovative approach allows exploration of a wide compositional range without dependence on pre-alloyed powders, significantly enhancing experimental flexibility. Moreover, this research systematically investigates nanosized boron additions for the first time, providing crucial insights into their effects on melt pool dynamics, solidification mechanisms, and microstructural evolution. Notably, fully refined equiaxed microstructures have been successfully achieved in trace boron-modified alloys, marking a substantial advancement in the field. Additionally, this study demonstrates, for the first time, the capability of the Resonant Acoustic Mixing (RAM) process to produce homogeneous satellite powder mixtures, offering a novel and reliable method for producing uniformly blended powders for PBF-LB/M. An analytical solidification model developed in this research further elucidates the complex relationships between PBF-LB/M processing parameters, boron content, and resultant solidification behaviours, offering a valuable predictive tool for optimizing microstructural characteristics.

Consequently, the novelty of this research includes: (i) pioneering the comprehensive investigation of nanosized boron additives in PBF-LB/M-processed Ti6Al4V-xB alloys, (ii) introducing a powder-free method for evaluating viable alloy compositions, (iii) achieving fully refined equiaxed microstructures at trace boron concentrations, (iv) the first demonstration of producing homogeneous satellite powder mixtures for PBF-LB/M process using RAM technique, and (v) establishing analytical and experimental microstructure-process mappings. These advancements collectively address key gaps, significantly enhancing the understanding and processing capabilities of boron-modified titanium alloys via PBF-LB/M.

CHAPTER 3

EXPERIMENTAL PROCEDURE

This chapter describes the experimental work involved in this research including materials, processing, and characterization techniques for PBF-LB/M of Ti6Al4V-xB alloy compositions. The experimental procedure chapter was divided into nine sections to discuss the methods used throughout this research. Section 3.1 includes the materials utilized in the PBF-LB/M and arc melting process. In this section, powder characterization techniques are discussed in detail. Section 3.2 gives details about a unique powder mixing technology to prepare the raw materials. Sections 3.3 and 3.4 describe the details of arc melting and PBF-LB/M sample production methods, respectively. The microstructure and crystallographic texture of the samples using these methods will be discussed in Chapter 5 and Chapter 6. Sample preparation for microstructural examination and description of material characterization techniques are given in Section 3.5 and Section 3.6, respectively. The methodology used for the reconstruction of the parent β phase is also reported in Section 3.6. Procedures for Archimedes' method for density measurement, microhardness test, tensile test and heat treatment procedure are also reported thru Sections 3.6 to Section 3.10.

3.1 Overview of the Methodology

This research systematically investigates the laser powder bed fusion and arc melting of Ti6Al4V-xB alloys to analyse their microstructure, mechanical properties, and in-situ grain refinement mechanisms induced by boron modified chemical composition of Ti6Al4V alloy. The methodology integrates material preparation, advanced manufacturing, post-processing, and multi-scale characterization techniques.

First, Ti6Al4V ELI powders with a powder size distribution of 15 – 45 μm and boron nanopowders in amorphous and crystalline form with a mean powder size of 70 – 80 nm were blended using Resonant Acoustic Mixing technique to ensure homogeneous distribution of boron nanopowders on micron size titanium powders. The blended powders were then processed via PBF-LB/M via Renishaw AM400 system with optimized critical parameters such as laser power, exposure time, and hatch distance to study in-situ grain refinement and arc melting under inert argon atmosphere to fabricate pre-alloyed samples with boron concentrations ranging from 0 to 2.5 wt.%B validate the effect of boron on solidification and grain refinement behaviour. Following fabrication, the samples underwent microstructural examination and phase analysis. This involved preparing metallographic cross-sections and

using techniques such as optical microscopy, SEM, EBSD, and TEM to identify grain size, phase constituents, and crystallographic orientation relationships. Specifically, the parent β phase was reconstructed from the room-temperature α phase data through EBSD data, allowing insights into high-temperature processing textures. Complementing the microstructural work, mechanical properties are evaluated using Archimedes' density measurements, microhardness tests, and tensile testing of both as-built and heat-treated specimens. Finally, heat treatment procedures—such as annealing cycles and ageing—were performed to assess changes in microstructure and mechanical responses. This multi-stage process ensures a robust correlation of how boron content and manufacturing parameters influence grain refinement, texture evolution, and overall performance of Ti6Al4V-xB alloys.

By uniting these steps—powder processing, arc melting, PBF-LB/M, microstructural characterization, and mechanical testing—the methodology provides a comprehensive path to evaluate the effects of boron additions on the microstructure and properties of additively manufactured titanium alloys.

3.2 Materials and Characterization Techniques

3.2.1 Ti6Al4V Powder

Plasma-atomized Ti6Al4V Grade 23 (known as ELI) powders supplied by Carpenter Additive with a size range of 15-45 μ m were used to produce all the reference samples and powder blends in this work. Table 3-1 reports the nominal chemical composition of the powders. Particle size analysis was performed to validate the particle size range and acquire insights into the particle size distribution (PSD). Furthermore, powder morphology was characterized using a JEOL 7100F Schottky Field Emission Scanning Electron Microscope (FE-SEM), coupled with an Oxford Instruments Advanced X-max 150 Energy Dispersive Spectroscopy (EDS) detector for comprehensive elemental analysis.

Table 3-1 Chemical compositions (in wt.%) of the Ti-6Al-4V ELI alloy supplied by Carpenter Additive.

Element	Chemical Composition (wt.%)
Titanium	Balance
Aluminium	5.50 – 6.50
Vanadium	3.50 – 4.50
Iron	≤ 0.25
Oxygen	≤ 0.13
Carbon	≤ 0.08
Nitrogen	≤ 0.05
Hydrogen	≤ 0.012
Yttrium	≤ 0.005
Other elements	≤ 0.10 each, ≤ 0.40 total

The particle size distribution was assessed using a Malvern Mastersizer 3000 via the laser size diffraction (LSD) method. Figure 3-1 illustrates the morphology of Ti6Al4V powder together with its particle size distribution and corresponding EDS maps of Ti, Al, and V. The laser size diffraction analysis encompassed a total of 10 cycles. The D (%) values were as follows: D10 at 22.1 μm , D50 at 33.2 μm and D90 at 48.9 μm . While the powder size range spanned 15-45 μm , particles >45 μm constituted 14.1% of the powder volume, with particles <15 μm accounting for 0.58%. From Figure 3-1, it is apparent that particles exceeding 50 μm in size are absent within the field of view. Distorted particles or agglomerates are not observed, which is expected considering the sample size. Moreover, all particles exhibit spherical forms without any indication of oxide scaling or satellite particles.

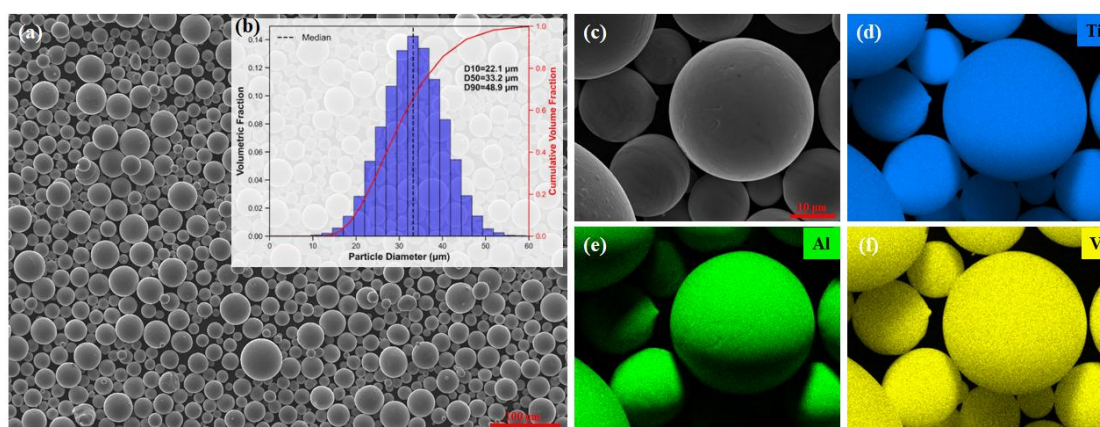


Figure 3-1 (a) SEM-SE micrograph showing the morphology of Ti6Al4V; (b) particle size and cumulative size distribution of the powder; (c) SEM-SE micrograph showing the region of interest with the (d-f) corresponding EDS maps of Ti, Al, and V.

3.2.2 Boron Nanopowders

Boron nanopowders (99.8%, metals basis) sourced from Nanoshel UK Ltd. were used to modify Ti6Al4V powders. The average particle size was reported as 70nm by the manufacturer. SEM images and TEM images from manufacturer of amorphous and crystalline nanoparticles are shown in Figure 3-2(a) – (f). Additionally, crystalline boron nanopowders with average particle size of 80nm from the same source were utilized in this study. The XRD patterns of both amorphous and crystalline boron powders, acquired using a Bruker D8 Advance DaVinci X-ray diffractometer and shown in Figure 3-2(e), distinctly highlight their respective crystallinity. The XRD pattern of the amorphous boron powder displays an amorphous hump and indicates 25% crystallinity, whereas the crystalline boron powder shows distinct peaks, indicating 90% crystallinity. This study utilized both amorphous and crystalline boron nanopowders to better understand the effect of crystallinity on grain refinement.

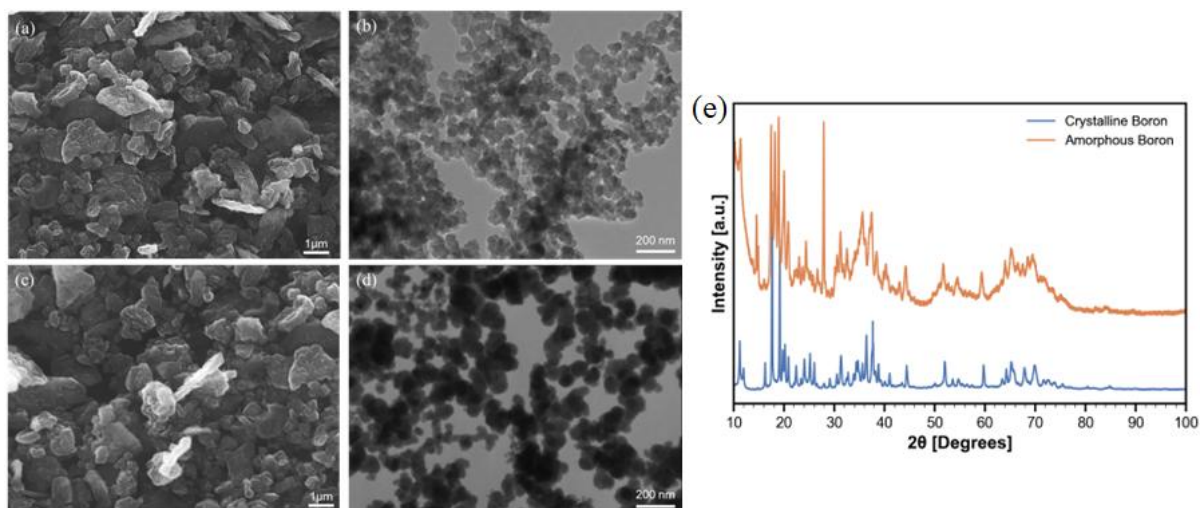


Figure 3-2 SEM-SE images of (a) Amorphous Boron nanoparticles; (c) Crystalline nanoparticles; and TEM image of (b) Amorphous; (d) Crystalline nanoparticles supplied by the manufacturer; (e) XRD pattern of powders.

3.2.3 Ti6Al4V-xB Powder Blends

Figure 3 3 illustrates the morphology of Boron-modified Ti6Al4V powder alongside with its particle size distribution and corresponding EDS maps of Ti, Al, V, and B. The laser size diffraction analysis encompassed a total of 10 cycles. The D (%) values were as follows: D90 at 48.9 μm , D50 at 33.2 μm , and D10 at 22.1 μm . While the powder size range spanned 15-45 μm , particles >45 μm constituted 14.66% of the powder volume, with particles <15 μm accounting for 0.69%.

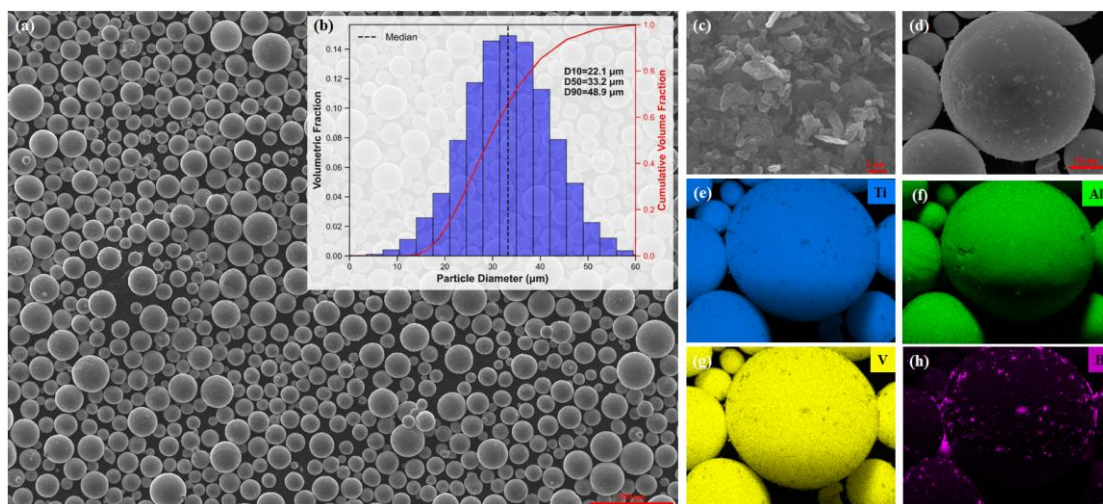


Figure 3-3 (a) SEM-SE micrograph showing the morphology of Ti6Al4V; (b) particle size and cumulative size distribution of the powder; (c) SEM-SE micrograph showing the morphology of Boron; (d) SEM-SE micrograph showing the region of interest (d) with the (e-h) corresponding EDS maps of Ti, Al, V and B.

3.3 Resonant Acoustic Mixing (RAM) Process

3.3.1 Description of Equipment

Resonant Acoustic Mixing (RAM) is a fast and unique mixing technique developed by Resodyn Acoustic Mixers. It involves applying high-intensity acoustic waves at a low resonant frequency (60 Hz) in a non-contact manner to achieve efficient mixing, as illustrated in Figure 3-4. The RAM process can be explained as a mass-spring-damper system where energy is transmitted between the spring and the moving mixing media in the vessel. Contrary to conventional mixing technology, in which the mixing focuses at the tips of the impeller blades, the RAM technology for acoustic mixing operates based on the principle of generating micro-mixing zones throughout the entire mixing vessel, allowing for a homogeneous mixing process. RAM technology can operate with multiple material types, such as liquid-liquid, liquid-solid, gas-liquid, or solid-solid systems. The design of RAM technology ensures that the mechanical energy of the mixer system is not lost to the materials being mixed through the transmission of an acoustic pressure wave in the mixing vessel (Andrews et al., 2020; Van der Walt, 2022). Acceleration is the main parameter that facilitates mixing in the LabRAM equipment. The device utilizes acoustic energy, through intense vibrations, to produce high shearing zones within the mixing vessel. By creating a high energy environment, the powders are almost fluidized, allowing sub-micron sized guest particles to collide with the host particles resulting in dry coated host particles.

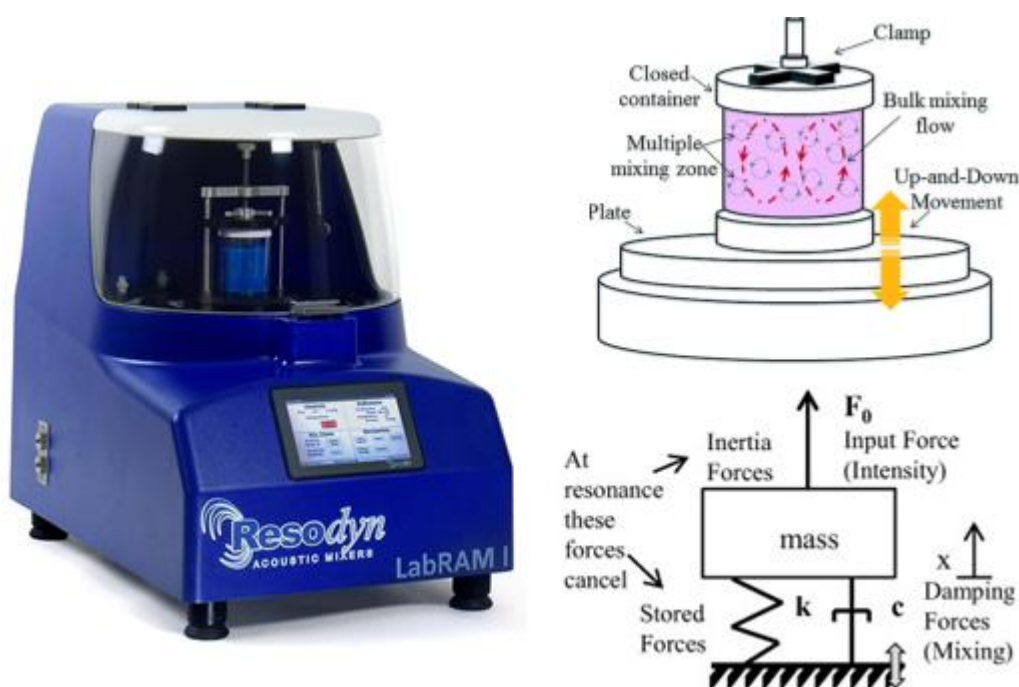


Figure 3-4 A bench top LabRAM I resonant acoustic mixer (left) and its mixing mechanism illustrating formation of micro mixing zones during the mixing process.

3.3.2 Materials and Process Overview

Plasma atomised Ti6Al4V powders with a particle size range of 15-45 μm provided by Carpenter Additive were modified by the addition of Boron nanopowders using LabRAM I resonant acoustic mixer shown in Figure 3-4. High purity (99.8%) Boron nanopowder with the average particle size (APS) of 70 nm was supplied from Nanoshel UK Ltd. In order to ensure complete mixing in a resonant acoustic mixer, a jar should be mostly full (~75%) with the raw materials to be mixed. Therefore, in a typical coating run, 400 grams of powder mixture consisting of 0.1 wt.% Boron nanopowders and 99.9 wt.% Ti6Al4V powders were poured in a plastic container with rounded internal edges. For all mixes undertaken, the raw materials were weighed directly into the container at the start of each mixing cycle. The closed container with the raw materials was secured in the resonant acoustic mixer, and then the pressure in each container was slowly reduced to 0.1 mbar in 15s before the start of the mixing process. A two-step mixing process was employed to ensure complete mixing of the raw materials. Initially, the raw materials were mixed at an intensity of 50G for 30-minute duration with 10-minute intervals. Following the initial 10-minute mixing process, the powder mixture was permitted to rest for a period of 20 minutes to dispel any accumulated heat.

3.4 Arc Melting Procedure

The alloys of interest were produced from cylindrical scrap Ti6Al4V produced by PBF-LB/M and 99.8% pure Boron nanopowders from Nanoshel UK Ltd. Prior to the arc melting operation, the nanopowders were compressed into pellets measuring about 1 mm in height and 10 mm in diameter using MSE PRO Lab Scale 15-Ton Manual Hydraulic Pellet Press in fume hood. To prevent powder pulverization by the electrical arc during the synthesis, it is essential to densify the powder mix as a vital step. Precision cutting machine was used to section the cylinder to a size of 2 mm in height and 9 mm in diameter to obtain desired weight. The sectioned Ti6Al4V pieces were ultrasonically cleaned in an isopropanol bath at room temperature for 3 minutes. Titanium sections and powder pellets were separately weighed in specific proportions with a precision electronic balance to an accuracy of 0.0001g in order to obtain various Ti6Al4V-xB alloys with compositions ranging from 0 wt.% to 2.5 wt.% and then were loaded and stacked in a densely packed manner on the water-cooled copper hearth, along with a CP titanium oxygen getter. Prior to the melting of each of the alloys and titanium getter, the arc melter chamber was purged under vacuum to a pressure of 10^{-3} mbar and backfilled with high purity argon. The process was repeated three times prior to melting to ensure the cleanliness of the arc melt buttons. After reaching the optimal vacuum level, the chamber filled with a research grade argon (N5.5) gas to achieve a working pressure of 0.7 bar. Water cooling was applied to the copper hearth while melting. The potentiometer was set at 6 for melting of the pieces. To discharge static electrons, an electric arc was ignited briefly by touching the plate with the electrode. The arc was first used to melt titanium getter to absorb any contaminations which may be still present, and then each alloy compositions were melted and held in a well-stirred molten state for of 50-60s to form a homogenous mixture. This button of alloy cooled down to a temperature when it no longer glows and was then flipped over in the chamber under

evacuated conditions. The melting and flipping process was repeated four times to convectively mix and uniformly distribute the alloying additions throughout the button. The nominal and calculated wt.% B for each button is shown in Table 3-2. Accurately determining the boron content can be challenging due to boron's low atomic number, reducing its X-ray emission efficiency and can introduce peak overlaps in conventional EDX spectra. To ensure the precision of boron measurements, additional WDX and ICP-OES analyses were performed on selected low-boron alloys up to 0.5 wt.%B. WDX offers higher spectral resolution by dispersing characteristic X-rays according to their wavelengths, thereby improving peak separation, while ICP-OES provides high-sensitivity solution-based elemental analysis and mitigates matrix effects. The close correspondence among the EDX, WDX, and ICP-OES results in these low-boron alloys confirmed that EDX could be reliably used for higher-boron samples. Furthermore, because the cooling rate in arc melting is strongly influenced by the mass of the sample, each alloy button was consistently produced from a total of 3 grams of feedstock. This standardized approach ensured comparable thermal histories across all compositions, thus minimizing variations in the resulting microstructures.

Table 3-2 Weights of Ti6Al4V bulk alloy and boron used to make buttons.

Nominal wt.% B	Nominal wt.% Ti64	Weight Ti64 (g)	Weight B (g)	Calculated wt.% B	Button Weight (g)
0	100	3.0769	0	0	3.0769
0.10	99.90	3.0542	0.0031	0.10	3.0573
0.20	99.80	3.0003	0.0066	0.22	3.0069
0.30	99.70	3.0096	0.0096	0.32	3.0192
0.40	99.60	3.0344	0.0124	0.41	3.0468
0.50	99.50	3.0459	0.0157	0.52	3.0616
0.60	99.40	3.0094	0.0181	0.60	3.0275
0.70	99.30	2.9896	0.0211	0.70	3.0107
0.80	99.20	3.0028	0.0243	0.81	3.0271
0.90	99.10	3.0271	0.0274	0.90	3.0545
1.00	99.00	3.0563	0.0310	1.01	3.0873
1.60	98.40	3.0177	0.0483	1.61	3.0660
2.50	97.50	3.0373	0.0765	2.51	3.1138

3.5 PBF-LB/M Processing

3.5.1 System Overview AM400

All the samples investigated in the present work were produced using a Renishaw AM400 (Renishaw PLC, UK). The AM400 is as the name suggests fitted with a 400 W ytterbium fibre laser, which has a 1070 nm wavelength and focused to a spot diameter of 70 μm . It can achieve a build rate of up to 20 cm^3/hour with a maximum laser scan speed of 2 m/s. The powder layer thickness can vary from 20 μm to 100 μm on average. The printing process occurs within an inert atmosphere formed by vacuum evacuation and argon gas filling, ensuring oxygen levels

remain below 0.1% in the chamber. To minimize consumption, gas is recirculated, and an additional gas flow safeguards the laser window from contamination. The AM400 is user-controlled via a touch screen located to the right-hand side of the chamber. The interface enables users to manage moving components during set up, clean down, and operation. Additionally, it allows tracking of build progress and sensor data such as temperature, pressure, and oxygen levels. To maintain the temperature of the optics system at 20°C, a chiller is available adjacent to the machine. The Renishaw AM400 utilizes a modulated wave laser system, where a single scan track is divided into multiple static exposures. This method leads to the influence of several parameters on the scan speed, differing from continuous wave laser systems. As illustrated in Figure 3-5, the spatio-temporal law linked to the optical process is depicted. In this approach, a scan track of variable length is segmented into discrete pulses based on the point distance (PD), representing the gap between successive irradiations.

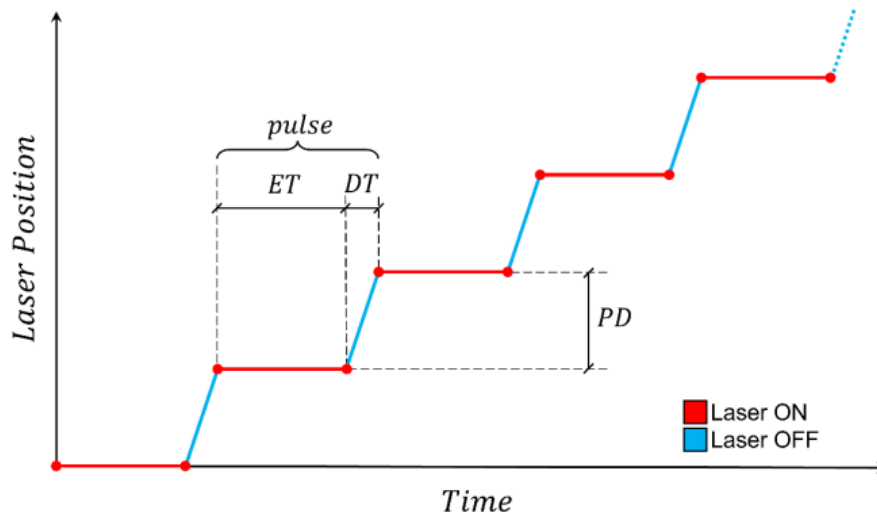


Figure 3-5 Laser spatio-temporal evolution associated to the Renishaw AM400 system(Del Guercio, 2023).

Each pulse comprises two temporal segments: the first involves the laser irradiating the powder bed, denoting the exposure time (ET), while the second entails the laser moving to the next firing position while being turned off, representing the delay time (DT). The overall laser scan speed (v) for a scan track results from the computation of the speed associated with a single total irradiation cycle. This relationship is expressed in Equation 2.19:

$$v = \frac{PD}{ET + DT} \quad 2.19$$

3.5.1.1 Reduced Build Volume (RBV) Environment

The Renishaw AM400 Reduced Build Volume (RBV) integrates a retrofit insert designed for conserving materials and expediting experimental material or process development cycles. The RBV setup encompasses a build volume (width $\times$ depth $\times$ height) measuring $80 \times 80 \times 64 \text{ mm}^3$, with a standard maximum build capability of $78 \times 78 \times 55 \text{ mm}^3$. In the RBV environment, powder

delivery employs a dosing piston that incrementally rises after each layer deposition. As the powder recoater passes over it, a thin material layer is distributed across the build plate. Figure 3-3 provides a visual of an ongoing print within the reduced build volume environment (left) and a screenshot of the build plate from the QuantAM software (right). The depiction outlines the powder spreading direction and gas flow. In the reduced build volume setup, the build plate cannot be preheated before the printing process due to RBV module limitations.

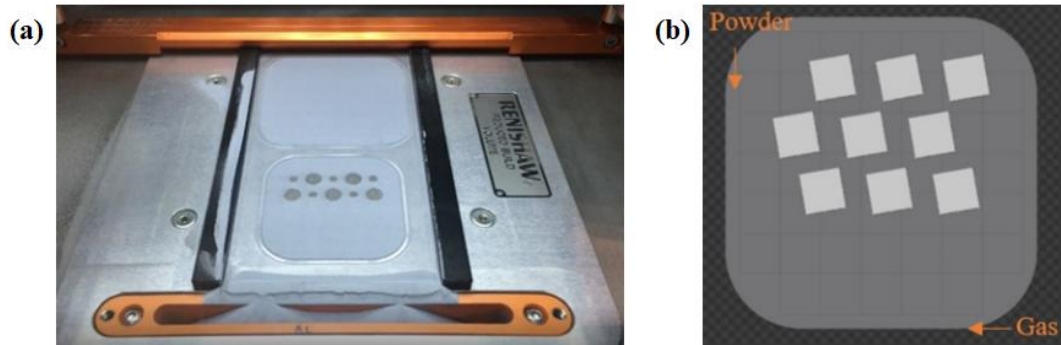


Figure 3-6 (a) Renishaw AM400 reduced build volume environment and (b) top view of the build plate when viewed in QuantAM software.

3.5.2 Process Steps

Before commencing the manufacturing process, the dosing area within the RBV apparatus was filled with Ti6Al4V-xB alloy powder, which was subsequently tapped to consolidate the particles. A substrate and rake were inserted and aligned in a parallel manner, maintaining a slight gap of approximately 50 μm to facilitate the initial layer deposition. The recoater blade of the raking system employs a 10mm diameter extruded silicone tube, replaced after each build. The entire process took place within a vacuum chamber. Upon initiating the build, the chamber was evacuated using a vacuum pump to achieve a pressure of 100 mbar. Subsequently, the chamber was purged with argon until the oxygen level reaches a predetermined threshold of 100 ppm. Notably, a heated build platform was not employed; the substrate begins the process at a room temperature of approximately 25°C. During manufacturing process, the initial powder was deposited from the dosing area located at the rear of the apparatus, ahead of the advancing rake. The rake deposited a powder layer onto the substrate. Any excess powder was directed into the overflow hopper at the front end of the apparatus. The selectively melted deposition, governed by a CAD file, occurred on the deposited powder. The substrate descended by the layer thickness, and the sequence was reiterated until the desired height was achieved. Upon completing a build, any remaining powder was brushed into the overflow hopper. The collected powder underwent sieving using a 53 μm test sieve to eliminate contaminants or large particles before reuse.

3.5.3 Software

Build files were prepared using a combination of Materialise Magics and Renishaw QuantAM software. Materialise Magics was employed to create a CAD file containing the desired geometry, which could be exported as an STL file for subsequent processing in Renishaw QuantAM software. Renishaw QuantAM software serves as a form of CAM software, enabling users to import a CAD model, specify process parameters, and slice the part according to the desired layer thickness. The software generates a computer code outlining the laser's scanning path and other machine controls. Moreover, the software generates laser paths for each layer based on a set of melt parameters. Subsequently, the slice and laser path data were exported as an MTT file, which was then interpreted by the AM400 equipment.

3.5.4 Laser Surface Melting of Ti6Al4V-xB Alloy Compositions

The laser of the Renishaw AM400 system was adopted to conduct laser surface melting and investigate the in-situ grain refinement of Ti6Al4V as a function of boron concentration and distinct melting regimes. A series of laser scan tests were carried out on the arc melted buttons. The flat surface of the buttons was melted line-by-line using parameters listed in Table 3-3 to replicate the deposition of a single-layer in PBF-LB/M, albeit without powder. In this work, a powder-free experimental methodology was employed on the surface of arc-melted buttons to identify Ti6Al4V-xB composition suitable for triggering the in-situ grain refinement in PBF-LB/M process by evaluating several different Ti6Al4V-xB compositions over a composition range from 0 wt.% to 2.5 wt.% B, with each composition tested on a standard processing parameter set for Ti6Al4V. On the other hand, modified parameter set was used to understand the effect of cooling rate on the grain formation for a fixed B concentration.

Table 3-3 Process parameters used for multiple-bead laser glazing of the Ti6Al4V-xB alloy buttons.

Parameter	Standard Set	Modified Set
Laser Power (W)	200	150
Point Distance (μm)	75	30
Exposure Time (μs)	50	30 – 120
Hatch Distance (μm)	65	65
Laser Focus (mm)	0	0
Platform Temperature (K)	298	298

3.5.5 Production of Ti6Al4V-xB Alloy Composition

Ti6Al4V and Ti6Al4V-0.1B alloy compositions were investigated to assess the in-situ grain refinement. Cubic samples with a 7 mm edge were produced with a powder layer thickness of 30 μm , using meander scan strategy with a rotation angle of 67° and 65 μm hatch distance. The point distance and delay time were kept constant at 30 μm and 20 μs , respectively, whereas the exposure time was changed to achieve difference in scan speed. The process parameters used to fabricate the Ti6Al4V-xB alloy samples is listed in Table 3-4.

Table 3-4 Range of powers and exposure times used to fabricate the Ti6Al4V-xB alloy compositions.

Parameter	Values
Laser Power (W)	150, 100
Point Distance (μm)	30
Exposure Time (μs)	30, 60, 90, 120, 150, 300, 450
Hatch Distance (μm)	65
Laser Focus (mm)	0
Platform Temperature (K)	298

3.6 Metallographic Sample Preparation

3.6.1 Sectioning and Mounting

Samples produced by arc melting and PBF-LB/M were sectioned in order to expose a surface parallel to the build direction, which is the z-axis. Sectioning was performed using Qcut 200 (Brilliant 220) precision abrasive cutter over the course of this work. The precision cutter was equipped with super thin silicon carbide bonded abrasive blade that sections the final cut surface without burning. All cuts were made at a maximum feed rate of 0.05 mm s^{-1} and a blade speed of 2500 rpm. All cuts were also continuously lubricated and were accurate to approximately 0.1 mm.

After the samples were sectioned, they are then mounted in a polymer for convenience in handling and protecting the edges. The sections were placed in the mounting cylinder of Opal 410 hot mounting equipment and then encased in a pre-measured amount of graphite filled conductive polymer powder. The mounting cylinder was then sealed, pressurised and heated. During mounting process, the pressure and temperature were held constant at 270 bar and 180°C , respectively, for 8 minutes to complete the polymerization process necessary to solidly encase the metal sections.

3.6.2 Grinding and Polishing

Grinding and polishing were carried out on a Struers Tegramin-25 and QATM QPol 300 automatic grinding/polishing machine. These operations on the mounted samples were performed in reference to the application notes suggested by Struers for titanium alloys. Three steps were performed for metallographic sample preparation utilising SiC grinding foil to produce a planar surface for roughly 2 minutes, a Struers MD-Largo composite disc for fine grinding for 10 minutes and a Struers MD-Chem polishing cloth for final polishing for 25 minutes or longer. Table 3-5 gives details of the metallographic sample preparation methods used during this study.

Table 3-5 Grinding and polishing procedure used during this study.

Process	Surface/Cloth	Suspension/ Lubricant	Force (N)	Speed (rpm)	Time (min)
Plane grinding	SiC Foil (P800)	Water	20	300	Until plane
Fine grinding	MD-Largo	9 μ m diamond	25	150	10
Polishing	MD-Chem	OP-S+10% H ₂ O ₂	30	150	25 (or longer)

The final step of the polishing was chemical-mechanical polishing with a mixture of colloidal silica (OP-S) and hydrogen peroxide (30% diluted) on Struers MD-Chem cloth. By introducing hydrogen peroxide, the reaction product between titanium and the silica suspension can be continuously eliminated, ensuring a surface free from mechanical deformation. Afterward, each part was individually cleansed using tap water, followed by drying with methylated spirits and a powerful stream of hot air.

Apart from the described metallographic preparation methods, the cross-sectioned surface of a sample for an EBSD measurement was prepared by subjecting it to a vibratory polish. The polishing rate was particularly slow in this instance, resulting in a process that lasted multiple hours. Mounted samples for vibratory polishing are secured in a sample holder to attain the necessary contact pressure on the polishing disk. Subsequently, the sample holder is positioned on a polishing cloth, which is dampened with OP-S+10% H₂O₂ suspension and moved over the cloth through vibrations. The VibroMet-2 vibratory polishing machine was utilized together with a chemical-resistant MicroCloth polishing cloth (Buehler) for the vibratory polishing procedure. To achieve the maximum CI index for the as-built samples, vibratory polishing was conducted for a minimum of 8 hours.

3.7 Material Characterization Techniques

3.7.1 Optical Microscopy

For optical microscopy imaging, a Nikon Eclipse LV100 ND microscope was utilized. This instrument was employed for both microstructural examination and porosity analysis of the samples. Various methods exist for evaluating the porosity of AMed parts, with the Archimedes' method and optical image analysis being among the most used. Prior research has shown the Archimedes' method can be effective, though it may have limitations when the relative density of the parts is very high. To complement the Archimedes' method and provide a more detailed assessment of pore morphology, optical measurement was also employed in this study.

To prepare for porosity measurement, images of polished but unetched samples were taken on planes parallel to the build direction. These images were then stitched together and cropped to uniform sizes to ensure consistency in the results. The stitched images were thresholded and converted to black and white. The relative porosity was calculated by determining the ratio of

black pixels (pores) to white pixels (solid metal). Additionally, the morphology of the pores was analysed to identify defect types. All steps, including image stitching and morphology examination, were conducted using the ImageJ software.

3.7.2 Scanning Electron Microscopy (SEM)

A Jeol 7100F Schottky Field Emission Scanning Electron Microscope (FESEM) equipped with Oxford Instruments NordlysMax3 electron backscatter diffraction (EBSD) detector and Oxford Instruments Advanced X-max 150 energy dispersive spectroscope (EDS) detector was employed to investigate powder morphology and microstructural features throughout this research. The SE imaging was used to depict fracture surfaces of specimen after tensile testing and microstructural features after chemical etching of the surface. To distinguish the individual phases, SEM images for microstructure investigations were typically obtained in the BSE mode. The additional EDS technology allows the analysis of chemical composition of individual microstructural components. After relatively short scanning times a qualitative and quantitative (except e.g., B, C, N and O) evaluation of components was obtained. Observation conditions can be found in Table 3-6.

Table 3-6 Analysis techniques and settings used for the microstructural characterisation.

Analysis	Electron Voltage (kV)	Working Distance (mm)	Probe Current
SE Imaging	15	10	Variable
BSE Imaging	5	4	Variable
EDS Analysis	15	10	12 nA
EBSD	15	16	5 nA

3.7.3 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) can provide information on the microstructure, crystal quality, and defect concentrations (with certain limitations). Moreover, diffraction patterns obtained during TEM analysis can provide data about crystal symmetry and lattice parameters, while the composition of the specimen can be determined through techniques such as EDX, Auger spectroscopy, and Electron Energy Loss Spectroscopy (EELS). TEM can provide information about the thickness, composition, and interfacial quality of each layer in multilayer specimens, while also revealing extended defects such as dislocations and stacking faults.

A JEOL 2100F and JEOL 2100Plus transmission electron microscopes were employed to investigate microstructural features throughout this research. Both microscopes operated in both TEM and STEM modes and an acceleration voltage of 200 kV. While JEOL 2100F is a field emission electron gun (FEG) instrument providing a high brightness and high stability electron source, JEOL 2100Plus is a multipurpose transmission electron microscope equipped with LaB6 source filament for high throughput and high versatility analysis. HRTEM was

performed on a JEOL 2100F FEG-TEM equipped with Gatan K3 IS camera, Oxford Instruments 80mm X-Max system for EDS analysis, and Gatan Tridiem Filter Spectrometer and 2K x 2K CCD camera, enabling elemental mapping via Electron Energy Loss Spectroscopy (EELS) analysis. BF, DF and STEM was performed on a JEOL 2100Plus equipped with Gatan OneView camera, Oxford Instruments X-MaxN 80 TLE EDS detector, and Gatan Enfium EELS detector. STEM/EDX maps for the elements of interest were recorded to analyse the microstructural features in the sample.

The first step carrying out a TEM analysis is to transfer the sample of interest effectively onto a TEM grid. Furthermore, as the name of the technique implies, TEM requires a thin enough specimen, allowing the electrons to transmit through. Among a variety of ways to prepare TEM samples, focused ion beam (FIB) milling is a useful method. TEM samples can be rapidly produced by the FIB lift-out technique from a site-specific region on a bulk sample or a particle. The TEM specimens employed in this study underwent meticulous preparation via the FEI Quanta200 3D dual beam focused ion beam (FIB) system, which utilizes Ga⁺ ions. These ions served three distinct roles: i) milling the sample, ii) providing protection and depositing an attachment layer of platinum (Pt), and iii) facilitating real-time monitoring of the preparation process. Pt protection layer deposition ensued through the simultaneous application of C₉H₁₆Pt gas and the ion beam onto the targeted region, resulting in the deposition of Pt atoms on the sample surface (Figure 3-7 (a)). Subsequent steps encompassed the ion beam excavation of three trenches within the sample, leaving a wall dividing the trenches, as illustrated in Figure 3-7 (b). The upper surface of the sample piece was encased in the Pt protection layer. The trench depths measured a few micrometres, with the wall thickness approximating 1.5 µm. Notably, during the Pt deposition and trenching phases, the sample surface remained perpendicular to the ion beam. The sample was then tilted to a 45° angle relative to the ion beam, facilitating the ion beam-mediated removal of a U-shaped piece from the sample wall, as depicted in Figure 3-7 (c). An almost complete severing of the sample piece occurred, leaving only a slender bridge intact on the left side of the sample piece. A micromanipulator, characterized by a sharp tip, was subsequently introduced near the sample piece (Figure 3-7 (d)). This enabled the attachment of the small sample piece (the lamella) to the micromanipulator through Pt deposition. The bridge was excised, and the lamella was delicately extracted from the wafer (Figure 3-7 (e)-(f)). Following this, the lamella was situated on a copper grid sample holder (Figure 3-7 (g)), undergoing a repeat Pt deposition process to secure attachment (Figure 3-7 (h)). The sample stage was once again rotated, aligning the top surface of the lamella perpendicularly to the ion beam. Finally, ion beam milling was employed to achieve the desired thickness of the TEM lamella, as shown in Figure 3-7 (i).

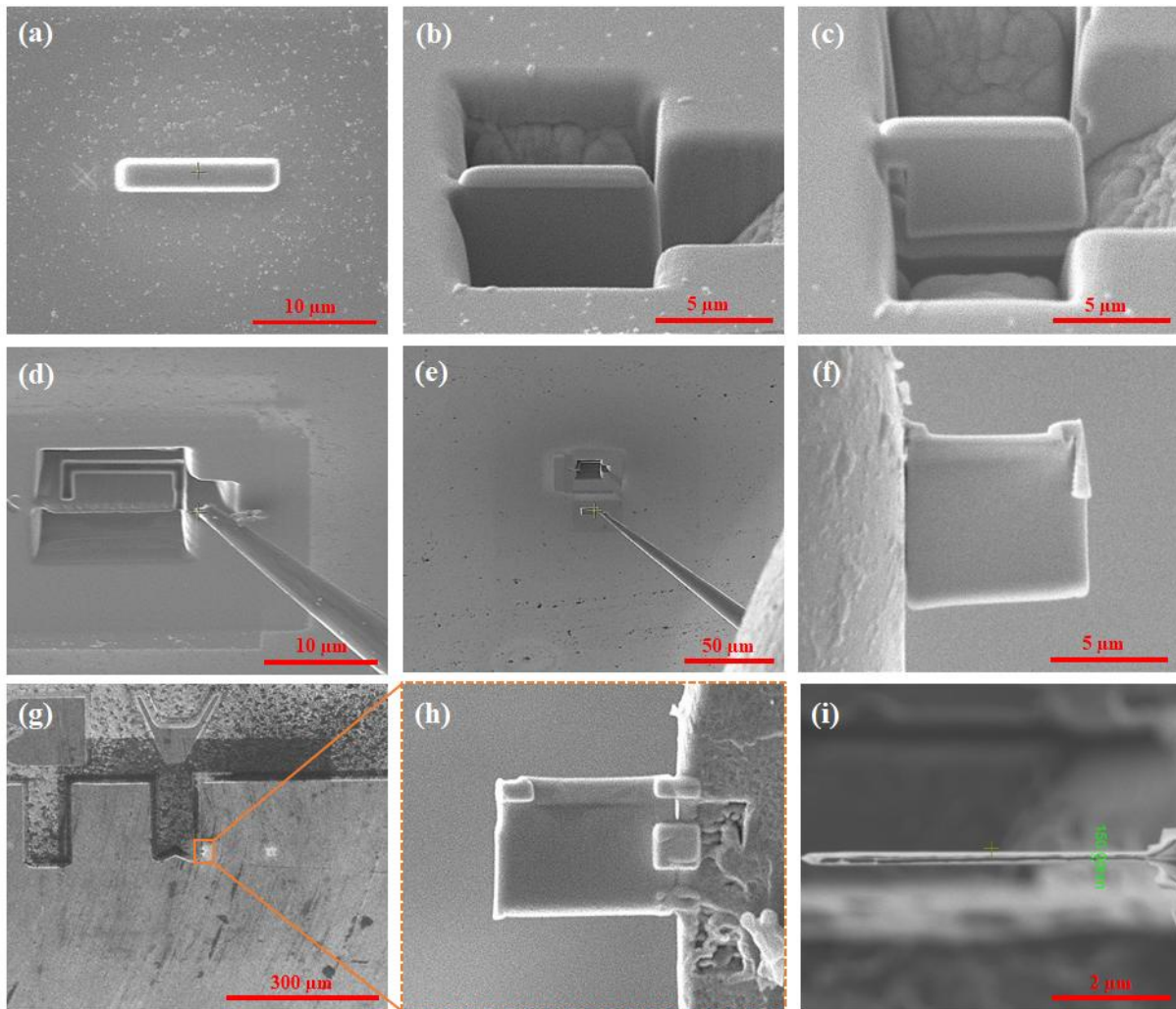


Figure 3-7 TEM lamella preparation by means of FIB: (a) Pt deposition on the region of interest; (b) milling of side tranches; (c) final stage of milling; (d)-(e) In-situ lamella welding and extraction using the micromanipulator inside the FIB/SEM chamber; (f) micrograph of the lamella attached on the micromanipulator; (g)-(h) Foil welding on copper lift-out grid, and (i) final milling sample to desired thickness.

3.7.4 Electron backscatter diffraction (EBSD) Technique

Electron backscatter diffraction (EBSD) has gained prominence in the last decade, primarily due to its enhanced capabilities as a fully automated technique (Kunze et al., 1993). In the realm of materials science research, it holds a significant role, offering valuable quantitative insights by revealing crystallographic orientations of near-surface crystals (Randle, 2009). Figure 3-8 illustrates the fundamental components of the EBSD system. This method concurrently provides a qualitative visualization of the microstructure, contributing to its wide utilization. The core of EBSD rests upon the angular dispersion of elastically backscattered electrons, positioning it as a method primarily cantered on surface analysis. The diffraction patterns formed by the primary electrons result in symmetry and lattice planar spacing data crucial for

determining the orientations of crystals serving as the diffraction source (Dingley & Wright, 2009). Typically, EBSD involves a raster scanning approach, where the user specifies a region on the sample and establishes a step size between discrete points, aligning them with a grid pattern within the designated area. During each data point acquisition, the crystallographic orientation is ascertained, and the corresponding angle information is archived. The customary practice involves illustrating the outcomes through a color-coded inverse pole figure (IPF) map (Essex, 2009), where distinct colours correspond to specific orientations, offering a distinctive microstructure visualization to the user. This two-dimensional depiction showcases only a fraction of the comprehensive information present within the stored dataset. This approach necessitates tilting of the sample, with challenges arising from the need to sustain focus across an extensive region due to fluctuations in the working distance—the gap between the sample and electron beam optics. Covering a sizable region like 1 mm², especially when combined with a diminutive step size ($\sim\mu\text{m}$), makes EBSD scans time-consuming, often stretching across several hours. Nevertheless, it remains a valuable approach for procuring quantitative insights into the microstructural features.

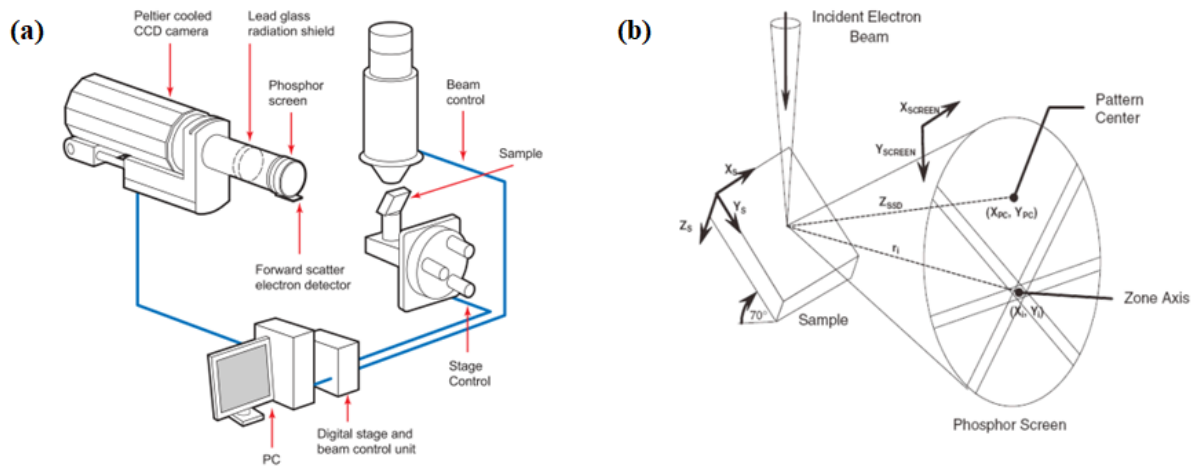


Figure 3-8 (a) Principal components of an EBSD system (Sydney et al., n.d.), and (b) Formation of Kossel-cones from divergent backscattered electrons incident on neighbouring Bragg planes of a tilted sample (Wynick & Boehlert, 2005).

A Jeol 7100F FESEM equipped with Oxford Instruments NordlysMax3 electron backscatter diffraction (EBSD) detector and Oxford Instruments Advanced X-max 150 EDX detector was used to determine the crystal orientation and grain sizes of PBF-LB/M manufactured Ti6Al4V-xB alloy compositions. When the beam of electrons was accelerated onto the 70° tilted sample surface, a diffracted pattern was formed on the phosphor screen of the EBSD detector. The flat screen displays a pattern, called the Kikuchi pattern, providing information about the grain boundaries and crystal orientations. In this study, the crystallographic features such as position of bands and indices of poles in the pattern were traced by a AZtec acquisition software. A probe current of approximately 5nA was established for the analysis across all the samples to be evaluated. The number of electrons diffracted is increased with a high probe current, which

enhances the quality of EBSD patterns, eventually increasing the indexing rate (Humphreys, 2001). Nevertheless, intensifying the current results in an enlargement of the beam dimensions, subsequently compromising spatial resolution. In this research, just like most studies on titanium alloys, acceleration voltage of 15kV was employed. Increasing the acceleration voltage and the probe current both detrimentally affect the spatial resolution; yet they enhance the indexing by producing patterns with higher contrast. Lowering the accelerating voltages may create challenges in generating viable EBSD patterns. The aperture size has also an effect on the resultant diffraction patterns and signal-to-noise ratio of EBSD. In general, enlarging the aperture size tends to improve a weak diffraction pattern, thereby increasing the indexing. In the course of EBSD analysis, an aperture size of 50 μm was selected to achieve optimal spatial resolution while conducting large area mapping. Step size is another factor affecting the indexing rate in such a way that a fine step sizes will result in higher indexing rates than a large step size. Therefore, 0.5 μm was chosen as an optimal step size to obtain approximately 80% of indexing rate and to determine microstructural features such as grain boundaries. In terms of influencing the resultant EBSD quality, the software parameters employed to ascertain individual point orientations encompass timing per frame, frame averaging, and the number of Kikuchi bands to detect. These three parameters significantly influence the outcomes. Timing per frame is optimized by considering the background and pattern quality, usually aiming for the lowest feasible value to boost acquisition speed. Employing longer frame times than necessary is generally counterproductive. Frame averaging can be advantageous when pattern quality is uncertain, potentially delivering more dependable results and subsequently elevating indexing rates. This study only required patterns with a maximum frame average of 2 frames. Choosing the maximum/minimum number of Kikuchi patterns to determine the solution for each acquisition point is crucial for achieving accurate crystal identification. A low parameter could result in inaccurate interpretations, undermining the overall reliability of the EBSD results. This research maintained a minimum of 10 bands, ensuring greater reliability in the results. Table 3-7 gives a definitive list of the parameters that can be changed together with the values deployed throughout the body of experimental work.

Table 3-7 Microscope and Aztec software operating parameters for EBSD measurement

<i>Parameters</i>	<i>Setup Conditions</i>
Electron Beam energy (kV)	15
Probe Current (nA)	5.00
Working distance (mm)	16
Aperture Size (μm)	50
Binned Pattern Size	4×4
Step size (μm)	0.50 – 0.53
Number of Bands	11
Hough Resolution	60

3.7.5 β -Grain Reconstruction

Since PBF-LB/M takes place in elevated temperatures, it is important to understand the crystallographic texture under high temperatures, particularly during the solidification process. Furthermore, it is crucial to ascertain the impact of the texture of the high-temperature phase on that of the low-temperature phase. Despite this, the high temperature β texture is obscured by the transformation α phase product owing to the β allotrope phase transformation. As documented in the literature, titanium undergoes an allotropic transformation at 882°C (for pure Ti). Upon cooling the alloy from the high-temperature β phase to room temperature, each BCC β grain transforms into HCP α platelets with 12 distinct feasible orientations (variants) relative to the parent β -grain. The transformation from β to α generally adheres to the Burgers orientation relationship of $\{110\}_{\beta}/\{0001\}_{\alpha}$ and $\langle 111 \rangle_{\beta}/\langle 11\bar{2}0 \rangle_{\alpha}$. Theoretical considerations suggest the presence of 12 potential variants or orientations during the $\beta \rightarrow \alpha$ transformation, dictated by the symmetry inherent in both phases according to the Burgers relationship. Conversely, the individual orientations of room temperature α -platelets, inherited from the β grain, can be utilized to compute the most likely orientation of the high-temperature parent β -grain. During an $\alpha \rightarrow \beta$ transformation, 6 potential variants exist in accordance with the Burgers relationship. Therefore, it is possible to calculate or reconstruct the β grain orientations for the parent based solely on the knowledge of room temperature α phase orientations by utilizing the Burgers orientation relationship.

The MTEX toolbox was used to analyse the raw electron backscatter diffraction (EBSD) data and to automatically reconstruct the high temperature β phase from the room temperature α phase in MATLAB. This toolbox automatically reconstructs the high-temperature EBSD map of a parent β -grain from the six potential variants of β during the $\alpha \rightarrow \beta$ transformation originating from the room temperature α phase. Each variant is individually reconstructed through its misorientation with neighbouring variants. Initially, the EBSD orientation data file for the room temperature α phase is cleansed to eliminate unindexed points. Subsequently, an algorithm calculates all conceivable β orientations by applying the Burgers relationship to each data point. Utilizing this data, the most likely β orientation for each α variant is determined, employing a minimum misorientation threshold of approximately 2.5°. To accomplish this, the initial step involves calculating the average orientation for each variant, yielding a set of 6 potential parent β orientations. These orientations serve as the benchmark against which solutions generated from the misorientation analysis can be compared, employing the method outlined by Humbert et al. (Gey & Humbert, 2003; Humbert et al., 1994, 1996, 2006; Humbert & Gey, 1999; Moustahfid et al., 1997). This process yields between 1 to 3 potential solutions for each pair of points. However, in practical scenarios, the majority of misorientations exhibit a solitary solution for the parent orientation. Whenever a solution derived from the analysed misorientation closely aligns with one of the 6 orientations within the reference set, the coincidence count for that reference orientation is incremented by 1. For each variant, the reference orientation boasting the greatest coincidence count is chosen as the accurate solution. Through iterative application of this method, the EBSD map of the high-temperature parent β -

grain can be reconstructed. Misorientations spanning boundaries that do not align with established variant misorientations are designated as β -grain boundaries. Notably, variant misorientations surpassing 4° during the reconstruction are recognized and designated as distinct prior- β grain boundaries (Gey & Humbert, 2002; Glavicic, Kobryn, Bieler, et al., 2003; Lonardelli et al., 2007). Data regarding the texture was taken from the initial measurements of α and reconstructed β , EBSD orientation maps. The information is presented in the form of standard pole figures.

3.7.6 X-Ray Diffraction

X-ray Diffraction (XRD) constitutes a robust technique employed for the investigation of polycrystalline structures through the examination of the interference pattern of X-rays scattered by electrons. During XRD experiments, the sample is subjected to illumination by a monochromatic X-ray beam at varying incident angles, denoted as θ , while detecting the diffracted X-rays at angle 2θ as depicted in Figure 3-9. XRD technique concentrates on the elastic scattering of X-rays, wherein diffraction does not result in any energy alteration, leading to the formation of Bragg peaks in the diffraction pattern that interrogate the long-range order of the structure.

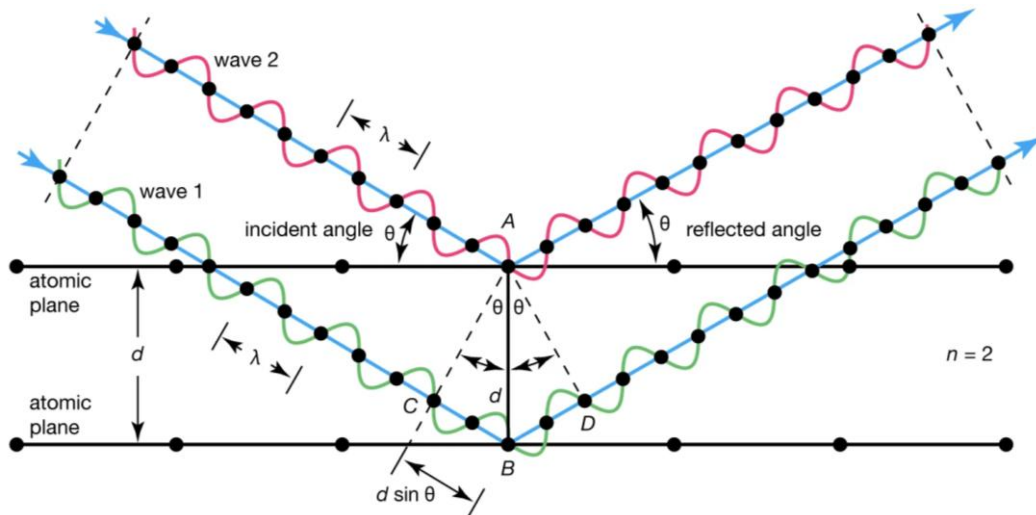


Figure 3-9 Schematic illustrating Bragg's Law and the derivation of interplanar d-spacing from diffraction of monochromatic X-rays (Encyclopaedia Britannica, n.d.).

Bragg's law (Equation 2.20) establishes the correlation between the wavelength of the incident X-ray radiation, λ , the d-spacing between parallel Miller planes, d_{hkl} , and the incident angle, θ , of X-rays. In Equation 2.20, n denotes an integer called the order of reflection

$$n\lambda = 2d_{hkl} \sin \theta \quad 2.20$$

Bruker D8 Advance DaVinci with a Bragg-Brentano geometry was employed to analyse any crystalline phase identification in both powder samples and PBF-LB/M manufactured

Ti6Al4V-xB alloy samples in this thesis. Prior to the XRD measurement of PBF-LB/M samples, the cross-sections (front view) were polished to 1 μ m to remove the possible oxide layer and to produce surfaces free from strain, induced by abrasive cutting. The diffractometer equipped with a Lynxeye 1D detector was set at 40 kV and 40mA to generate a Cu K α radiation (wavelength, $\lambda=0.15406$ nm). X-ray patterns were generated at multiple angles of 2 θ ranging from 20 to 95° with a step size of 0.01°, and 10-seconds counting time per data point. Due to the polychromatic nature of the radiation generated by the X-ray tube, background noise removal and K α_2 radiation stripping were performed using DiffracEVA software. Phase identification was performed by matching diffracted peaks from the experimental scan spectrum with phase patterns in the International Centre Diffraction Database (ICDD) to identify the corresponding diffracted peaks. In addition to the room temperature XRD measurements, in-situ high-temperature XRD (HT-XRD) experiments were carried out to determine the phase fractions experienced during the heat treatment cycle used in this research. Due to the high affinity of titanium alloys to oxygen, the specimens shielded in a vacuum chamber. It should be noted that the maximum operating temperature for HT-XRD is restricted by the decrease in vacuum stability and increase in tendency for oxidation at higher temperatures. D8 Advance series 2 was employed for all the HT-XRD measurements with a heating stage installed. Experiments were conducted at high temperatures using the same parameters as those employed in room temperature experiments.

3.8 Archimedes' Method for Density Measurement

The Archimedes method involves employing an analytical balance (Kern ABT100-5NM) and a density kit to determine the mass of a solid object both in air and when submerged in a specific fluid, such as water or acetone. For this study, an analytical balance with a high precision of 0.001 mg was utilized, along with an enclosure housing the density kit. The density kit consists of a beaker and a dual weighing pan frame, enabling measurements of specimen mass in both air and the chosen fluid of known density. To estimate the density of the fluid, its temperature is closely monitored during the measurements. Meanwhile, the air density is assumed to be 0.0012 g/cm³. In this study, distilled water served as the fluid used for immersion. Further details of the method can be found in the ASTM B311 standard (ASTM International, 2017). Water has poor wetting properties. Therefore, without the use of a wetting agent and/or smooth sample surfaces, it is possible for air bubbles to stick to the submerged solid body or gem holder, referred to as the wire basket holding the samples. Due to their buoyancy, air bubbles could impact the results. A bubble as small as 1 mm in diameter can cause 0.5 mg of buoyancy, while a bubble with a 2 mm diameter can lead to as much as 4 mg of buoyancy. Due to this problem, all sample surfaces were smoothed with SiC to eliminate the surface bubble formation upon immersion. Each sample was measured five times consecutively to determine the average relative density. After each wet measurement, the sample was carefully dried, and the balance was tared to 0 before the next dry measurement was made.

3.9 Microhardness Assessments

Measuring material hardness is a simple and effective way to obtain an initial impression of its mechanical properties at room temperature. Considering the limited sample dimensions, microhardness testing provides great potential in determining representative values for microstructure hardness. Micro indentation was conducted according to EN ISO 6507-1:2018 (International Organization for Standardization, 2005), using a Vickers pyramid indenter with a 5N (HV 0.5) force and a 10s dwell time. The measurements were carried out by creating a sequence of at least thirty indents per samples placed at discernible intervals within the material, in order to eliminate the impact of dislocation pile-up among the indents and grain boundaries, and also in proximity to neighbouring indents. The distance between the centres of neighbouring indents should be at least three times the diagonal length of the indent. The indents were made using the Wilson VH3100 automatic microhardness tester (Buehler), which was equipped with the DiaMet™ software for direct and easy hardness value evaluation. The Vickers hardness is calculated using the projection left by the Vickers indenter with included angles of 136° according to the following equation:

$$HV = 0.102 \frac{F_i}{A_{HV}} = 0.102 \frac{2F_i \sin\left(\frac{136^\circ}{2}\right)}{d_{HV}^2} \approx 0.1891 \frac{F_i}{d_{HV}^2} \quad 2.21$$

where F_i is the indentation load and A_{HV} is the projected indent area, which is described by the pyramid's diagonal d_{HV} (International Organization for Standardization, 2005).

3.10 Tensile Test Setup

Two types of tensile samples were employed for investigation of tensile properties of PBF-LB/M Ti6Al4V-xB alloys. The first type of samples was manufactured from vertically built cylindrical rods which had a diameter of 9 mm and a length of 52 mm. The cylinders with a diameter of 4 mm and a gauge length of 20.4 mm were machined into tensile specimens in accordance with the proportional dimensions specified in ASTM E8/E8M (ASTM International, 2022). The second type of samples were manufactured from rectangular bars built in both horizontal and vertical directions, with dimensions of 52mm x 14mm x 4mm (length x width x thickness) and then machined into the final shape with the gage length of 16 mm and the thickness of 2 mm according to ASTM E8/E8M standard (ASTM International, 2022). Figure 3-10 shows the final shapes of PBF-LB/M produced tensile test specimens.

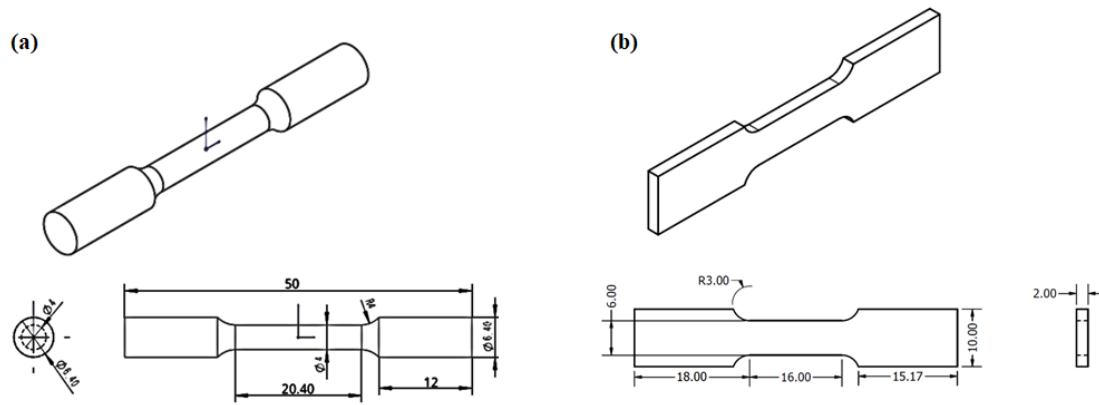


Figure 3-10 The final shape of PBF-LB/M-produced tensile test specimens is shown in (a) subsize dog-bone shape and (b) subsize flat shape.

The vertically built cylindrical test samples were tested to analyse the effect of different crystal structures on the mechanical properties in the as-built condition. Horizontally and vertically built flat tensile test specimens were employed with and without a heat treatment to analyse the effect of possible in-situ grain refinement on the mechanical responses. It is noteworthy that the potential oxide layer that may be formed during the heat treatment operation was completely removed. According to AMS2801B, a metal removal of 0.39 mm is required for complete oxide layer removal in Ti6Al4V subjected to the heat treatment at 1038°C for 1 hour in an air environment. Therefore, the removal of 2 mm of metal in this study should be more than enough.

The tensile tests were conducted at room temperature (20°C) with a strain rate of 0.14 mm/min using an Instron 5969 testing machine, which was equipped with a 50 kN load cell. The strain rate was chosen in accordance with ASTM B348-13 (ASTM International, 2013). The initial elongation of the gauge area was monitored using a video extensometer. When the elongation exceeded the threshold value, which was 3% for as-built specimens and 9% for the heat-treated specimens, the testing apparatus tracked the remaining elongation up to the point of fracture. The loading direction was perpendicular to the build direction of horizontally fabricated samples and parallel to that of vertically produced samples.

3.11 Heat Treatment Procedure

All conventional heating processes in this study were conducted using an LTF12 bench top tube furnace manufactured by Lenton Furnaces. The furnace used in the study was a commercial tube furnace which has a heating capacity of up to 1200°C and a maximum output power of 3kW. The furnace is equipped with a Eurotherm 2416 multiple program controller, which was used to regulate the temperature and heating rate. A constant heating rate of 10°C/min was applied throughout all the conventional heating processes. The specimens were heated to the desired temperature in a controlled manner. The heating rate was monitored using a thermocouple that was attached to the specimen. After the desired temperature was reached, the

specimens were soaked for a period of time to allow for homogenization of the temperature. The specimens were then cooled in a furnace at a rate of approximately 7°C/min. The process sequence for the conventional heat treatment used is illustrated in Figure 3.2. The figure shows the temperature profile of the specimen during the heating, soaking, and cooling stages. The figure also shows the average cooling rate during air cooling. The heat treatment process for the samples was based on the recommendations of ASTM and SAE standards (SAE International, 2014; ASTM International, 2021; ASTM International, 2014; SAE International, 2024). The annealing step was performed at 925°C for 2 hours. This step was used to relieve the stresses in the samples and to achieve a uniform microstructure. The aging step was performed at 700°C for 4 hours. This step was used to precipitate the alloying elements and to improve the mechanical properties of the samples. While the annealing process helped to improve the ductility, the aging process also helped to improve the strength of the samples. Therefore, with this designed heat treatment cycle, it is planned to obtain materials with high flexibility and strength. Oxidation is a common problem during heat treatment, as it can lead to the formation of a brittle oxide layer on the surface of the material, preventing the material from achieving its full potential strength and ductility. To prevent oxidation, all samples were heat treated under a research-grade argon atmosphere which ensures that the furnace atmosphere was free of oxygen. The furnace was purged with a high argon flow (5L/min) for 20 minutes before the heat treatment cycle began. This ensured that the furnace was completely filled with argon and that any residual oxygen was removed. During the heat treatment cycle, the argon flow was reduced to approximately 1.5 L/min to maintain an oxygen-free atmosphere. The argon flow was controlled using a mass flow controller throughout the heat treatment cycle to ensure that the oxygen content remained low. The samples were also visually inspected after the heat treatment cycle to confirm that they had not oxidized.

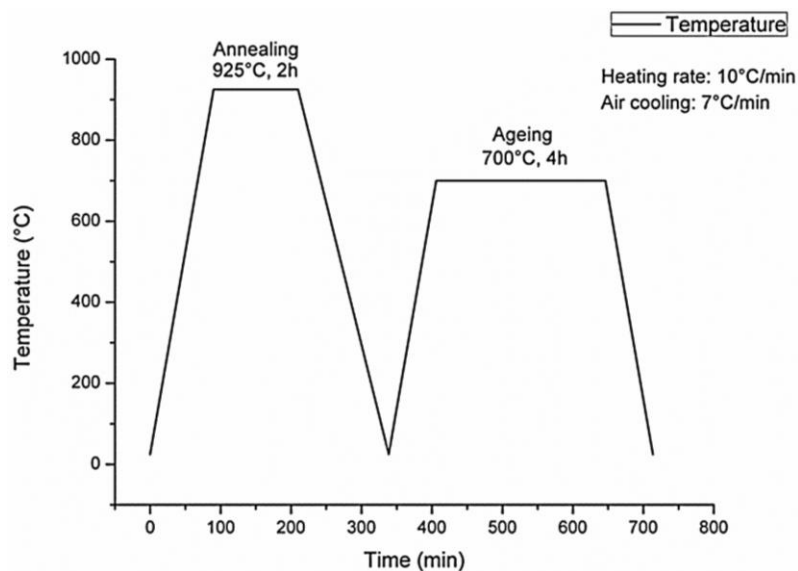


Figure 3-11 The process route for the applied conventional heat treatment.

The two-stage heat treatment for PBF-LB/M processed Ti6Al4V-xB alloy was engineered to overcome the strength-ductility trade-off inherent to additive manufacturing while capitalizing on boron's grain-refining capabilities. During the 925°C solution treatment, metastable α' martensite—formed due to rapid solidification in LPBF—dissolves into the β matrix, while in-situ TiB precipitates pin prior- β grain boundaries, suppressing coarsening and retaining a fine-grained microstructure despite high-temperature exposure (DebRoy et al., 2018; Z. Liu et al., 2021). This stabilization enables dissolution of α' without sacrificing grain boundary integrity, a critical advantage over conventional Ti6Al4V, where uncontrolled β grain growth occurs above 850°C (Dutta & Froes, 2016). Subsequent 700°C annealing facilitates controlled α -phase globularization via dislocation recovery and β -phase precipitation at subgrain boundaries, with TiB particles accelerating elemental diffusion to promote uniform α spheroidization (Jiang et al., 2020; Sabban et al., 2019). The resultant bimodal microstructure—comprising equiaxed α -phase for ductility and fine lamellar α/β colonies for strength—achieves a synergistic balance of mechanical properties (UTS: 1050–1100 MPa, elongation: 12–15%), surpassing single-step annealed LPBF Ti6Al4V (elongation ~10%) (Z. Sun et al., 2016; Thijs et al., 2010). Crucially, dual role of TiB precipitates as a grain refiner and diffusion pathway modifier eliminates the need for multi-cycle treatments used in other titanium alloys, streamlining the process while mimicking thermomechanically forged microstructures. This approach not only mitigates AM-induced anisotropy but also enhances fatigue resistance by reducing stress concentrations at prior- β grain boundaries, positioning Ti6Al4V-xB as a viable candidate for high-performance aerospace and biomedical applications (S. Zhang et al., 2022; Z. Zhao et al., 2018).

CHAPTER 4

BORON-INDUCED GRAIN REFINEMENT IN Ti6Al4V: FROM ARC MELTING TO PBF-LB/M

4.1 Introduction

As a mold-free manufacturing method, AM provides flexibility in part geometries allowing customization to be exploited to an exceptional degree especially for high-end applications in aerospace, aviation, and biomedical industries. Titanium offers a superior specific strength, mainly because it is lower in density than most other high-performance structural metals such as steels. The strength, stability, and resistance to oxidation of the alloy can be further improved by α -stabilizing elements such as aluminium, oxygen, nitrogen, and carbon, and/or β -stabilizing elements, like molybdenum, vanadium, and tantalum. This alloying process results in various titanium-based alloys categorised as α , $\alpha+\beta$, and β alloys based on their microstructure at room temperature (L. M. Kang & Yang, 2019). Integration of titanium and its alloys with AM facilitates the fabrication of lightweight structures, essential for lowering fuel consumption, in vehicles and enhancing comfort in biomedical applications (Batalha et al., 2022).

Despite the benefits of AM with titanium and its alloys, several challenges remain. The layer-by-layer fabrication inherent to metal AM techniques creates a substantial thermal gradient along the growth direction during fabrication. This directional cooling and steep thermal gradients often result in the microstructure of titanium-based components exhibiting pronounced columnar growth of β -grains along the build direction (M. J. Bermingham et al., 2015). When cooled below β -transus temperature without stabilization, the primary- β phase transforms to the α -phase. During this solid-state phase transformation, the growth of grain boundary α and other α morphologies is typically governed by prior- β through the orientation relationships (Germain et al., 2007). This generally causes AMed titanium and its alloy parts to develop a strong texture, resulting in anisotropic mechanical properties. For example, the grain boundary α phase, aligning with the columnar prior- β grains, acts as a preferred pathway for crack propagation, potentially causing premature failure (Carroll et al., 2015). Accordingly, the ductility under tensile load is generally much lower in the transverse direction, i.e. perpendicular to the build direction, compared to the longitudinal direction, i.e. parallel to the build direction (Kok et al., 2018). According to Zhang et al. (K. Zhang et al., 2019), large columnar prior- β grains cause anisotropic effects on the fatigue crack growth rate due to cracks

preferentially propagating along grain boundaries. Additionally, repeated reheating during the addition of new layers promotes grain growth, causing coarse grain morphologies (M. J. Bermingham et al., 2015), negatively impact several mechanical properties. For example, although coarse microstructures may achieve higher toughness and fatigue crack growth threshold due to the tortuosity of crack tips in larger grains, fine-grained materials generally demonstrate superior unnotched fatigue performance compared to coarse-grained materials (Sen et al., 2007). Similarly, large prior- β grains encourage the formation of large α -colonies, i.e. clusters of neighbouring α -laths with the same orientation, where the tensile strength of titanium is inversely related to the α colony size (K. Zhang et al., 2019).

Two strategies have been proposed to enhance microstructural homogeneity: promoting a less textured β -grain microstructure through the columnar-to-equiaxed transition and/or manipulating the α -phase to achieve grain refinement and eliminate undesired variants like grain boundary α or large colony α (M. J. Bermingham et al., 2018). The extensive knowledge previously obtained from titanium and titanium alloy casting is being leveraged to control the microstructure of AMed components by incorporating trace elements like boron, silicon, and beryllium. Among these, boron is recognised as an exceptional grain refiner for titanium and its alloys (G. Singh & Ramamurty, 2021), due to its unique ability to promote constitutional supercooling and growth restriction (M. J. Bermingham, McDonald, Dargusch, & StJohn, 2008; M. J. Bermingham, McDonald). Boron is also highly effective in preventing unfavourable α -variants, with as little as 1000 ppm of boron being sufficient to eliminate grain boundary α in Ti6Al4V casting (Roy, Suwas, et al., 2011). In addition to the grain refinement and texture weakening induced by boron, the reactions between boron and titanium lead to the formation of non-oxide intermetallic phases like TiB, TiB₂ and Ti₃B₄. These phases are refractory materials known for their high stiffness and excellent thermal stability (J. D. Avila & Bandyopadhyay, 2019; Gorsse et al., 2003). Boride-reinforced titanium matrix composites (TMCs) offer a number of advantages, including enhanced strength and hardness (R. Banerjee et al., 2004c). Furthermore, TiB-reinforced TMCs demonstrate improved creep resistance, as the thermally stable TiB particles inhibit the plastic flow of grains and/or phase boundaries at elevated temperatures. When TiB precipitates grow in-situ within individual titanium grains, they can also restrict the mean free path of mobile dislocations (L. Huang et al., 2021). It is of the utmost importance to achieve a uniform dispersion of TiB in the matrix to increase creep resistance (R. Banerjee et al., 2004). Zhou et al. (Z. Zhou et al., 2023) conducted creep tests on parts produced by PBF-LB/M and demonstrated the addition of just 1.18 wt.% of TiB₂ (resulting in the formation of 2 vol.% of TiB) significantly improved the creep resistance of Ti6Al4V. Further improvements were observed following heat treatment of the as-built parts due to increased α/β interfaces acting as barriers to dislocation motion.

Among various reinforcements, TiB has attracted considerable attention due (J. D. Avila & Bandyopadhyay, 2019) resistance (J. D. Avila & Bandyopadhyay, 2019) and poor wear performance of titanium (Y. Hu, Ning, et al., 2018). Eutectic TiB grows as single-crystal nanowhiskers within the matrix, and its elongated, needle-like morphology provides substantial

reinforcing effect. Consequently, even a small amount of TiB can significantly improve the stiffness and surface properties of titanium, including wear resistance (Chandran & Panda, 2002; M. Y. Koo et al., 2012; Morsi & Patel, 2007; Tamirisakandala et al., 2006). These acicular reinforcements also contribute to the toughening of the composite through mechanisms like crack bridging (S. Wei et al., 2013). TiB is thermodynamically stable in titanium (J. A. Otte, Zou, et al., 2022) and inhibits grain growth at high temperatures, even above the β -transus (Tamirisakandala & Miracle, 2012). The closely matched thermal expansion coefficients (S. Wei et al., 2013) effectively reduce residual stresses at the Ti-TiB interface (Y. Hu, Ning, et al., 2018a; Tamirisakandala et al., 2006b). Furthermore, the similar densities of titanium and TiB (J. A. Otte, Soro, et al., 2022; J. A. Otte, Zou, et al., 2022) enable TiB to enhance the stiffness and strength of titanium and its alloys without increasing weight, offering significant weight-saving advantages over the alloy (Tamirisakandala & Miracle, 2012).

Due to the extraordinary chemical and thermal stability of TiB within the titanium (Gorsse et al., 2003), it is theoretically possible to create TiB-reinforced TMCs both ex-situ and in-situ. Conventional procedures, such as mixing raw titanium powders with TiB particles and then treating them using powder metallurgy processes, have been effective in demonstrating the ex-situ method (Kondoh, 2015). Conversely, the in-situ approach is predominantly employed in AM. Strong interfacial bonding is encouraged by the clean interface that in-situ generated reinforcements provide with the surrounding matrix (Das et al., 2012; S. Wei et al., 2013). On the other hand, impurities at the interface in ex-situ composites might erode the interfacial bonding, making the secondary particles act more as rigid inclusions than useful reinforcements (Dadbakhsh et al., 2019). Furthermore, compared to conventional manufacturing, the high cooling rates commonly seen in AM result in a substantial refinement of in-situ formed TiB and other reinforcements, limiting the formation of massive intermetallics serving as stress concentration sites (R. Banerjee et al., 2004). Given the strict restriction of ASTM F2924 (ASTM International, 2021) for the composition of Ti6Al4V components generated by PBF, the efficacy of boron in modifying the microstructural properties of titanium and related alloys, even in trace amounts, is critical. Elements like aluminium, vanadium, iron, oxygen, carbon, nitrogen, hydrogen, and yttrium have specific tolerances established for them, whereas all other elements are restricted to a maximum of 0.1 wt.% each, with a combined total limit of 0.4 wt.%. Accordingly, microstructural modification can only be accomplished by element additions in trace levels (M. J. Bermingham et al., 2018). However, identifying the ideal or required quantity of boron in titanium and its alloys produced using AM remains a challenging task. Zhang et al. (K. Zhang et al., 2019) discovered adding trace amounts of boron (≤ 1.0 wt.%) was sufficient to induce CTE transition of prior- β grains, eliminate undesirable α forms like grain boundary α , and promote the formation of refined α -laths with a reduced aspect ratio and weakened texture. Nonetheless, Zhang et al. (K. Zhang et al., 2019) also reported a steady decrease in ductility with increasing boron content, ultimately recommending an addition of 0.05 wt.%B to achieve balanced tensile properties. In another study, He et al. (Y. He et al., 2019) used a powder-free PBF-LB/M method, in which single tracks were laser-scanned in arc-melted buttons, to investigate the combination of Ti6Al4V and Boron across a broad compositional range up to

10 wt.%B. They tested 14 different sets of laser power and scan speed for each composition, generating 70 single scans. From their analysis, He et al. (Y. He et al., 2019) concluded boron contents between 2 and 5 wt.% were promising for Ti6Al4V composite parts manufactured by PBF-LB/M. This range produced a large processing window, a stable melt pool comparable in size to unmodified Ti6Al4V, and a desirable microstructure characterized by a TiB network with submicron spacing.

While research is growing in the literature, the optimal concentration of boron for microstructural manipulation of AMed titanium-based parts is still missing. To bridge this gap, the present research provides a critical examination of the microstructural evolution in Ti6Al4V-xB alloy through arc melting and laser irradiation of arc-melted buttons. A powder-free approach, simulating a laser-deposited melt pool on surface of a bulk alloy to reasonably approximate the melt pool formed during PBF-LB/M, was used to evaluate microstructural variations. Various alloy compositions were laser-irradiated with fixed parameters, resulting in melt pools of different sizes, microstructures, and hardness. The resulting microstructures provided insights into the effectiveness of boron for grain refinement in PBF-LB/M process. This research enhances understanding of microstructural evolution in Ti6Al4V and related alloys under rapid solidification, offering strategies for improving alloys for AM. Gaining a deeper understanding of Boron-induced microstructural changes appears to be critical for the wider adoption of AMed titanium-based components in industry, taking into consideration the importance of improving their mechanical behaviour in performance-critical applications. The ability to manipulate grain structure through strategic alloying, as demonstrated in this study, can enhance material properties such as strength and fatigue resistance. Consequently, our findings contribute to the understanding of microstructural evolution in PBF-LB/M processes and the development of superior PBF-LB/M materials.

4.2 Assessment of Arc-Melted Ti6Al4V-xB Alloys

4.2.1 Microstructure Analysis

The representative SEM images of arc melted Ti6Al4V-xB buttons can be seen in Figure 4-1(a) – (f). The grey, white and black contrast in backscattered SEM images of alloy microstructures indicate α , β , and TiB phases, respectively. Ti6Al4V Figure 4-1(a)) showed a typical Widmanstätten microstructure with a lamellar microstructure of $\alpha+\beta$ and α_{GB} . Microstructures of all Ti6Al4V-xB alloy compositions showed $\alpha+\beta$ colony microstructure with alternate layers of hexagonal close-packed (hcp) α and thin body-centred cubic (bcc) β distributed in prior- β grains. In these structures, plate type $\alpha+\beta$ laths are oriented along preferred orientations per Burger's orientation relationships between β and α phases to form colonies. Several of these colonies are randomly oriented within a single prior β grain. The α -laths intersect each other like that of a typical basket-weave structure. As in-situ synthesized TiB was formed in Ti6Al4V matrix, the prior- β grain size and α -lath thickness was severely reduced. TiB whiskers tended to self-assemble into a network structure with a discontinuous distribution due to the insufficient content of TiB for alloys up to 0.4 wt.%B. With increasing boron concentration,

TiB whiskers showed a necklace-like equiaxed network arrangement as shown in Figure 4-1(g). The continuous coarse grain boundary α_{GB} and large grain boundary α colonies are present in base alloy. However, the presence of TiB significantly altered all variants of the α -phase, including α_{GB} . The coarse α_{GB} become discontinuous or even disappear as a result of the discontinuous distribution of TiB. Furthermore, The TiB precipitates exhibited two different morphologies: high-aspect-ratio whiskers and highly-faceted rods with hollow centres filled with titanium-matrix (Figure 4-1(f)).

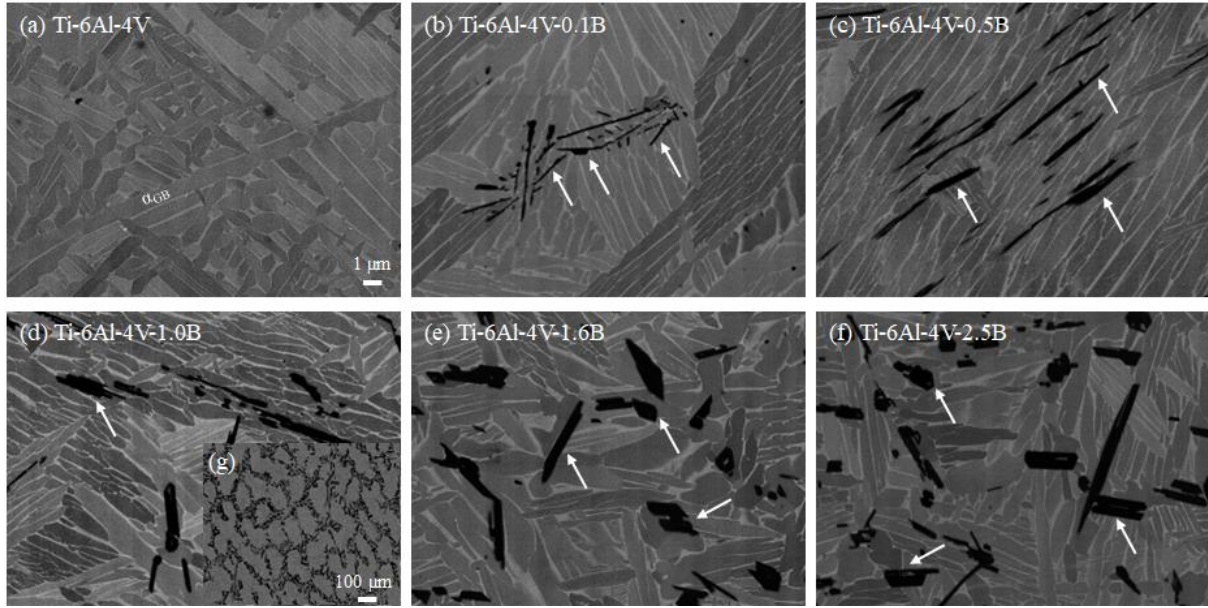


Figure 4-1 Representative SEM-BSE images of arc-melted microstructure for Ti6Al4V-xB alloy buttons of six different trial compositions: Ti6Al4V-0B, 0.1B, 0.5B, 1.0B, 1.6B, 2.5B, shown in (a), (b), (c), (d), (e), (f) respectively; and (g) Necklace-like network structure of TiB. White arrows indicate TiB precipitates.

Figure 4-2 presents the interfacial structure among the TiB, lamellar α and interlamellar β -phase in the arc melted Ti6Al4V-1.0B alloy. The TiB whisker, highlighted with a red rectangular box, exhibited a thickness of approximately 10nm with high aspect ratio of 96 and was in-situ synthesized adjacent to the interlamellar β and lamellar α (Figure 4-2(a)). Furthermore, the characteristics of the matrix microstructure adjacent to the TiB whiskers varied along its length. On the left side of the whisker, the long and narrow α -phase contained more dislocations (Figure 4-2(b)), with the interlamellar β -phase oriented approximately perpendicular or parallel to the TiB whisker. However, near the middle of the TiB whisker (Figure 4-2(c)), β and α phases containing more dislocations were located at the TiB boundaries. The selected area electron diffraction (SAED) patterns (Figure 4-2(d)) revealed the orientation relationship of $(0001)_{\alpha} \parallel (001)_{TiB}$, consistent with previously reported orientation relationship (Ozerov et al., 2017a). Additionally, TiB grew preferentially along the $[010]$ direction, resulting in a needle-like morphology. Due to the lower surface energies of the (101) and (100) planes compared to the (001) and (100) planes, TiB grew more rapidly in these directions (M. Fang et al., 2021; W.

J. Lu et al., 2008), thus forming the hexagonal cross-section (plate-like TiB) depicted in Figure 4-1(e) and (f). Figure 4-2(e) and (f) display the strong interfacial bonding of α -Ti/TiB and β -Ti/TiB without any reaction products. The crystal planes of $(11\bar{2}0)_{\alpha\text{-Ti}}$, $(010)_{\text{TiB}}$ and $(1\bar{1}0)_{\beta\text{-Ti}}$ were identified based on the calculated interplanar spacing of α -Ti (0.1473 nm), TiB (0.3099 nm) and β -Ti (0.2324 nm). Moreover, the orientation relationship of $(11\bar{2}0)_{\alpha\text{-Ti}} \parallel (010)_{\text{TiB}}$ and $[0001]_{\alpha} \parallel [001]_{\text{TiB}}$, as well as $(010)_{\text{TiB}} \parallel (1\bar{1}0)_{\beta\text{-Ti}}$ and $[001]_{\text{TiB}} \parallel [110]_{\beta\text{-Ti}}$, were determined. These results and analyses indicated the arc-melted alloys exhibit similar interfacial features and orientations to traditional cast and forged titanium matrix composites. However, the TiB whiskers in the arc-melted alloys present a fibrous morphology with nano-thickness, particularly observed near the surface in contact with the cold crucible. Additionally, α -phase showed a long and narrow morphology with more dislocations, attributed to the relatively rapid melting and solidification processes of arc melting.

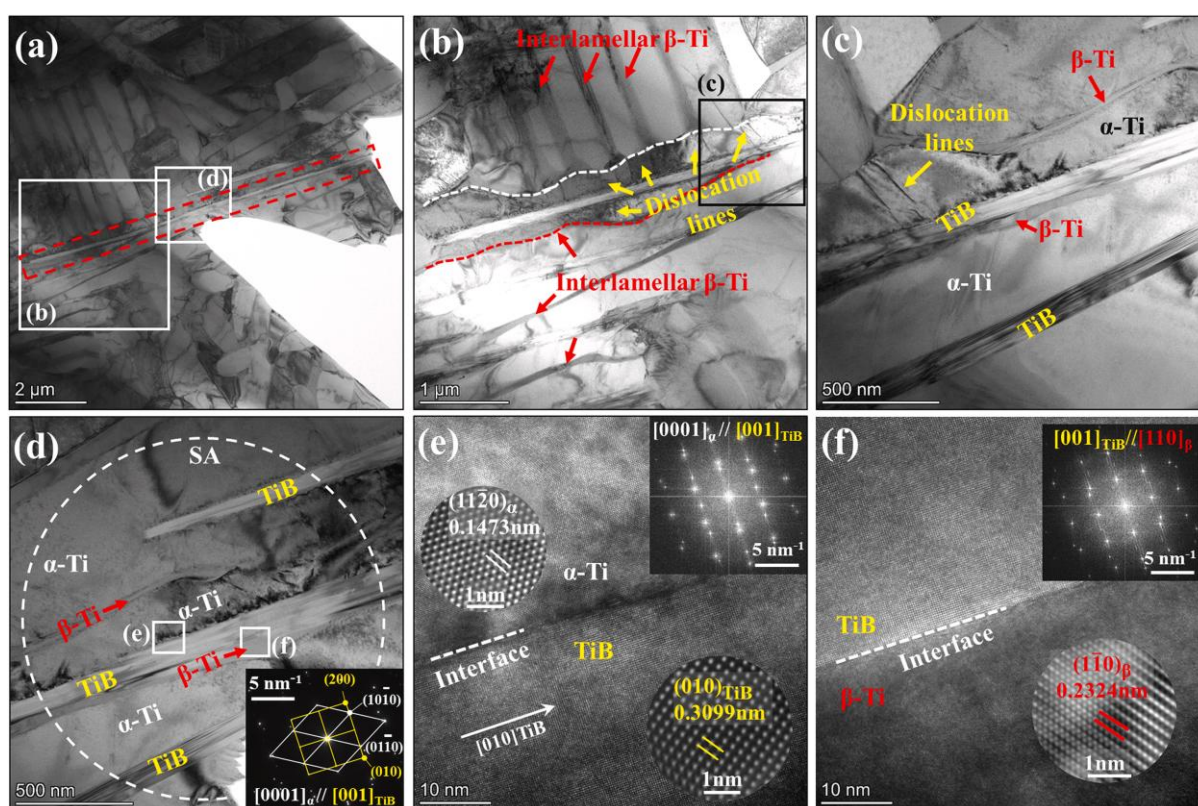


Figure 4-2 TEM images of the arc melted Ti6Al4V-1.0B. (a) – (d) depict the lamellae ($\alpha+\beta$) and TiB whiskers; high resolution TEM of the (e) α -Ti/TiB and (f) β -Ti/TiB interfaces along with the corresponding fast Fourier transform (FFT) and inverse fast Fourier transform (IFFT) patterns derived from (d).

4.2.2 Hardness Analysis

The effect of boron addition on the average hardness of Ti6Al4V-xB alloy compositions at a load of 500g is systematically depicted in Figure 4-3. The data demonstrated a clear linear enhancement in hardness with respect to boron concentration. This relationship indicates that

for every 1 wt.% increase in boron concentration, the average hardness increases by approximately 39 HV. The hardness values observed range from approximately 356 HV at 0 wt.%B to nearly 492 HV at 2.5 wt.%B.

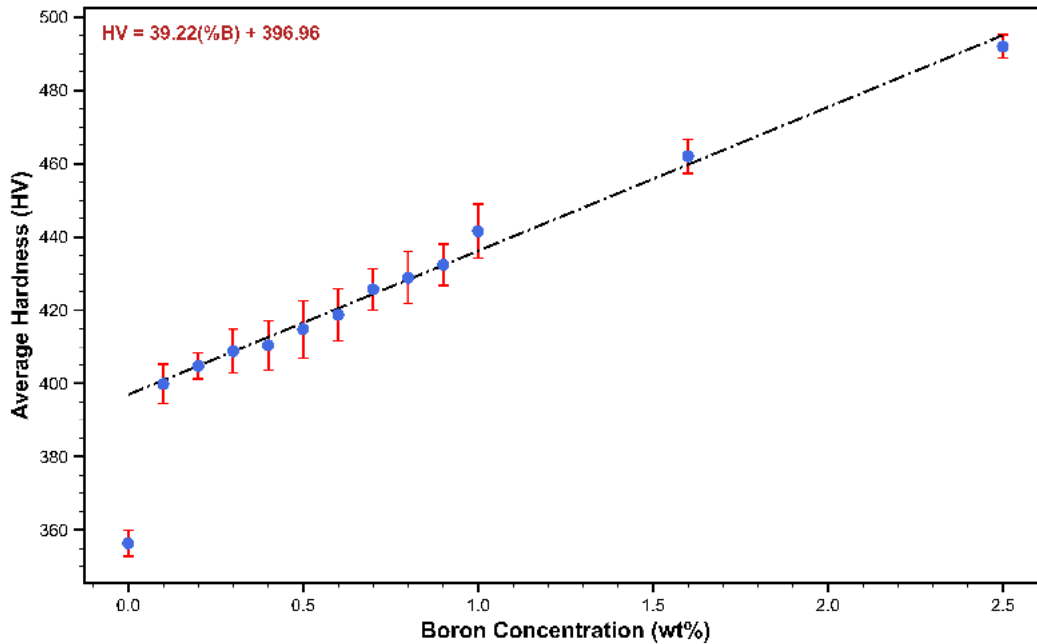


Figure 4-3 Variation of average microhardness values of Ti6Al4V-xB alloy compositions as a function of boron addition.

Additionally, nanoindentation was performed on each phase of the alloy to further investigate the mechanical properties. Representative load vs. depth of penetration curves from individual phases of Ti6Al4V-xB alloys are shown in Figure 4-4. Among the three phases present in the microstructure, TiB exhibited the highest stiffness, while the β -phase was the most compliant. The average elastic modulus for the TiB phase is 384.5 ± 40.2 GPa. The observed variation in elastic modulus was attributed to the anisotropy of the TiB needles. TiB possesses a complex orthorhombic B27 structure, characterized by zigzag chains of boron atoms parallel to the [010] direction (Decker & Kasper, 1954). This pronounced anisotropy in crystal structure results in the needle-like morphology of TiB and significant differences in the elastic moduli along the longitudinal and transverse directions. Due to the challenges associated with synthesizing single-crystal TiB (Ravi Chandran et al., 2004), several research teams have employed an indirect approach to approximate E_{TiB} by analysing experimentally determined moduli of Ti-TiB composites (Atri et al., 1999; Fan et al., 1994; Gorsse et al., 2003; Gorsse & Miracle, 2003; Ravi Chandran et al., 2004). Notably, Atri et al. reported a value of 371 GPa for E_{TiB} , which is in close agreement with the results presented in this research (Atri et al., 1999).

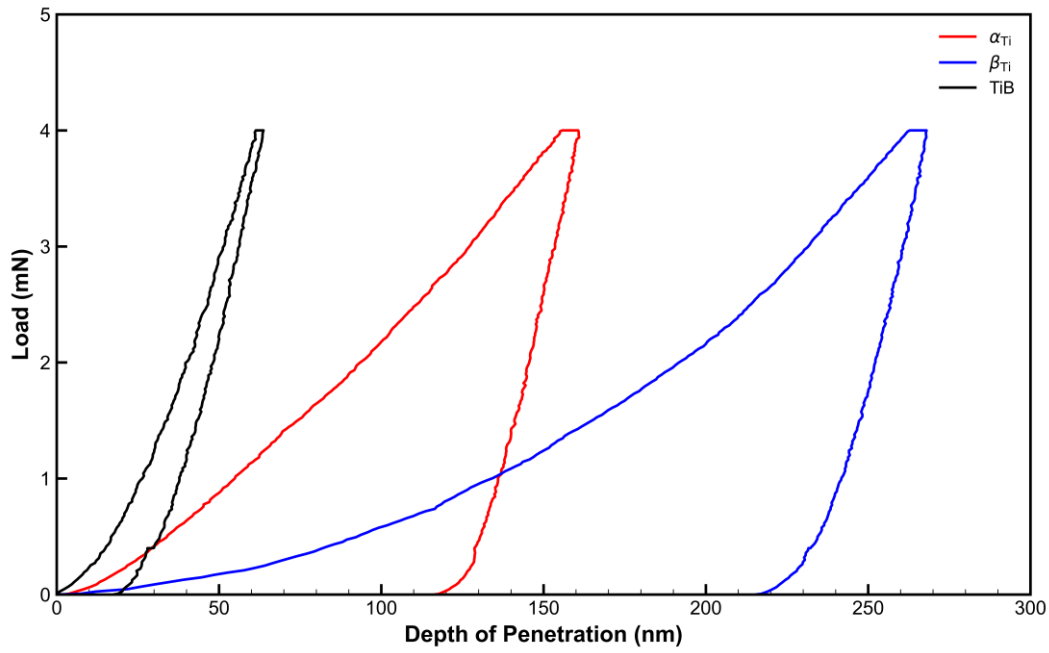


Figure 4-4 Representative load vs. depth of penetration curves for α , β and TiB phases present in Ti6Al4V-xB alloys

The average modulus values measured from 40 indentations for each phase were 132.2 ± 12.2 GPa for the α phase (E_α) and 81.1 ± 13.1 GPa for the β phase (E_β). No clear trend was observed linking these modulus values to boron content, indicating that boron dissolved in the alloy did not significantly impact the elastic modulus. The higher modulus of the α phase compared to the β phase was expected, given that α phase has a closely packed hexagonal close-packed structure, whereas β phase possesses a less densely packed body-centered cubic crystal structure. It is noteworthy that multiple researchers have previously reported modulus values for the α and β phases in Ti6Al4V alloys through both experimental and theoretical approaches (Fan, 1993b; A. Kumar et al., 2008; Y. T. Lee & Welsch, 1990). Particularly, experimental studies by Elfer et al. provided an empirical equation to calculate E_β based on the alloy composition expressed in weight percent as follows (D. Banerjee et al., n.d.):

$$E_\beta \text{ (GPa)} = 73 + 0.48V + 1.0Al + 1.5Cr + 2.0Mo \quad 4.1$$

Based on the chemical composition of the arc melted alloy, Eq. (x) estimates E_β to be around 80.9 GPa, which aligns very well with the nanoindentation data obtained in this study. Kumar et al., using atomic force acoustic microscopy, directly measured E_α and reported values of 121.1 GPa for (100) and (110), 142.7 GPa for (001), and 130.3 GPa for (101) (A. Kumar et al., 2008). The E_α values determined by nanoindentation here are reasonably consistent with the average of those measurements.

After evaluating all available data, it is aimed now to explain the observed experimental trend in Young's modulus as a function of boron concentration, shown in Figure 4.5. Initially, the possibility of predicting the experimental modulus of Ti6Al4V alloy without boron addition, denoted as E_{Ti64} , was estimated using the known modulus values for α and β phases (E_α and E_β). Given that the alloy microstructure is composed of colonies containing alternating α and β layers aligned along specific orientations, the modulus of a colony in directions parallel ($E_{||}$) and perpendicular ($E_{\perp}$) to these laths can be estimated using iso-strain and iso-stress models, respectively, as follows:

$$E_{||} = (V_\alpha \times E_\alpha) + (V_\beta \times E_\beta) \quad 4.2$$

$$E_{\perp} = \left(\frac{(E_\alpha \times E_\beta)}{(V_\alpha \times E_\beta) + (V_\beta \times E_\alpha)} \right) \quad 4.3$$

In the expression above, V_β denotes the volume fraction of the β phase, calculated simply as $(1 - V_\alpha)$. Given that the colonies exhibit random orientations within the microstructure, one would expect the elastic modulus of Ti6Al4V, E_{Ti64} , to be roughly the average of $E_{||}$ and $E_{\perp}$. Accordingly, the calculated value for E_{Ti64} is about 124.5GPa, while the experimentally measured value is 113GPa. This difference indicates that assuming a completely random distribution of α/β colonies might not accurately reflect reality. Therefore, to better capture the actual microstructural conditions, a correction factor R is introduced which is roughly 0.907. Therefore, E_{Ti64} can be calculated as follow:

$$E_{Ti64} = R \left(\frac{E_{||} + E_{\perp}}{2} \right) \quad 4.4$$

The variation in the elastic modulus as a function of boron concentration is shown in Figure 4-5. An increase (approximately 3%) in E is observed with the addition of 0.1 wt.%B. A steady increase in E was noted with further additions of boron. A linear variation of E with respect to boron concentration was observed, as highlighted with a dashed line in Figure 4-5. The upper bound estimate of the elastic modulus for boron-modified alloys can be expressed by the following equation (Sen & Ramamurty, 2010):

$$E = \left\{ \left(\frac{E_{||} + E_{\perp}}{2} \right) \times (1 - V_{TiB}) \right\} + \{ S \times V_{TiB} \times E_{TiB} \} \quad 4.5$$

where S represents the reinforcement efficiency factor of TiB needles on the overall modulus of the system. The estimated values of E , assuming $S=1$, computed using the equation, are plotted in Figure 4-5. The estimated value of E matches reasonably well with the experimental values for up to 0.3 wt.%B alloy. However, the estimated E is lower than the average experimental value for rest of the alloy compositions. While within the error limits up to 0.3

wt.%B alloy, the equation underestimates the modulus significantly for the higher boron-modified alloys. Microstructural observations accompanying these modulus measurements revealed important insights into the source of the discrepancy. Specifically, increasing boron content markedly reduces grain size and decreases the α -phase fraction. Moreover, the TiB phase progressively forms a continuous, interconnected "necklace" structure at grain boundaries (clearly illustrated in Figure 4-1(g)). Such a continuous network of TiB significantly enhances the overall stiffness beyond predictions based on conventional analytical approaches, which typically assume discrete and randomly dispersed reinforcements. Hence, the upper-bound estimation, employing an iso-strain assumption (i.e., $S=1$), systematically underestimates the experimentally determined modulus values at elevated boron levels. Additionally, it is possible that boron alters the effective orientation factor, R , which accounts for how α and β colonies are distributed and how they share load under mechanical stress. Minor variations in the arrangement or connectivity of these phases can cause disproportionately large changes in modulus—particularly when TiB serves as a bridging or continuous phase. The clear divergence between the estimated and experimental data at higher boron concentrations underscores the necessity for refined modelling frameworks, explicitly accounting for morphological transitions—particularly the transition to continuous TiB reinforcement. Future modelling approaches may require adjustments to the reinforcement efficiency factor, considering non-ideal strain-transfer conditions, percolation-like reinforcement behaviour, and modified load-sharing characteristics associated with the distinct grain-boundary TiB morphology observed at high boron contents. In summary, although iso-strain and rule-of-mixtures approaches offer a useful baseline for estimating alloy stiffness, they fall short when discontinuous reinforcements (like TiB) form networked or boundary-encompassing morphologies. The higher-than-anticipated stiffness values measured in alloys above about 0.3 wt%B highlight the significant influence of these interconnected stiff phases, as well as the possibility that boron modifies the effective orientation factor. Addressing these complexities requires advanced modelling, detailed microstructural characterization, and targeted experimental studies to fully explain—and ultimately harness—the marked stiffening observed in high-boron modified titanium alloys.

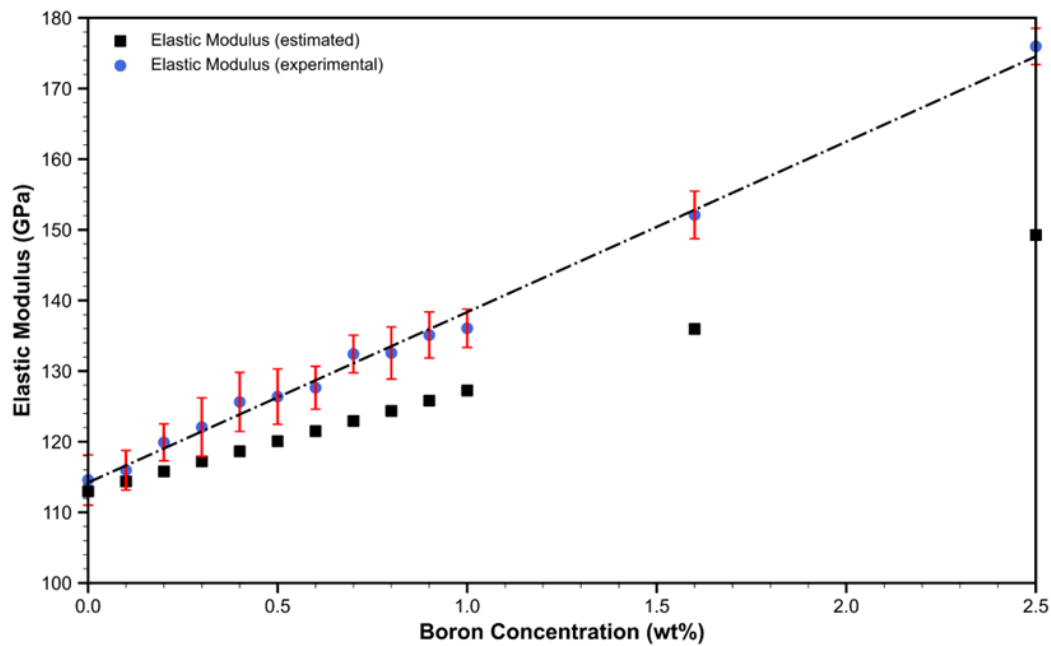


Figure 4-5 Variation of Elastic modulus, E , of the Ti6Al4V- x B alloys with respect to boron concentration. Dashed line is the best linear fit for the experimental values.

4.2.3 Phase Identification and Analysis

The XRD patterns shown in Figure 4-6(a) reveal that Ti6Al4V and Ti6Al4V- x B alloy buttons are mainly composed of hexagonal close-packed (hcp) titanium (α/α' -Ti). Trace amounts of boron addition caused a redistribution of the α/α' peak intensities as well as the presence of $\{110\}_\beta$, $\{200\}_\beta$ and $\{220\}_\beta$ peaks indicating that β -Ti phase is retained in the specimens. Meanwhile, as depicted by the Scheil-Gulliver solidification model from pseudo-binary phase diagram, the presence of the titanium boride (TiB) phase with B27 orthorhombic crystallographic structure was also confirmed by XRD characterization. Figure 4-6(b) and Figure 4-6(c) give the enlarged view of XRD patterns within the 2θ ranges of $23^\circ - 30^\circ$ and $41^\circ - 58^\circ$ to indicate the B27 orthorhombic TiB and $\{200\}_\beta$. There is no indication of the presence of residual boron in the Ti6Al4V- x B alloy buttons. This suggests that the initial boron present in the mixture has been completely converted into TiB phase. Although the atomic radius of B is smaller than Ti, the addition of B does not cause the obvious lattice distortion of the α and β phases, thus the peak position of the α and β phases does not change with increasing B content. It is interesting to note that there are more peaks of α and β phases corresponding to different crystal planes are detected with the increasing B content which is the indicative of a more chaotic orientation of the α and β phases. Generally, base Ti6Al4V alloy showed peaks with lower intensities and smaller widths than the boron modified alloy buttons. According to the Scherrer equation, the crystallite size can be correlated directly with the peak width, and in extremely small crystals, only a few repeating lattice planes exist to enforce the Bragg condition; therefore, a broader angle of incident X-rays is reflected without suppression by destructive interference, i.e., smaller crystallites produce broader peaks. Despite these valuable

considerations, further studies to be conducted by either Rietveld analysis or Hall-Williamson method are required to comprehensively differentiate potential causes of peak broadening since XRD peak broadening may happen due to several phenomena, such as, micro-strains caused by high dislocation density or other defects in the crystal structure, etc.

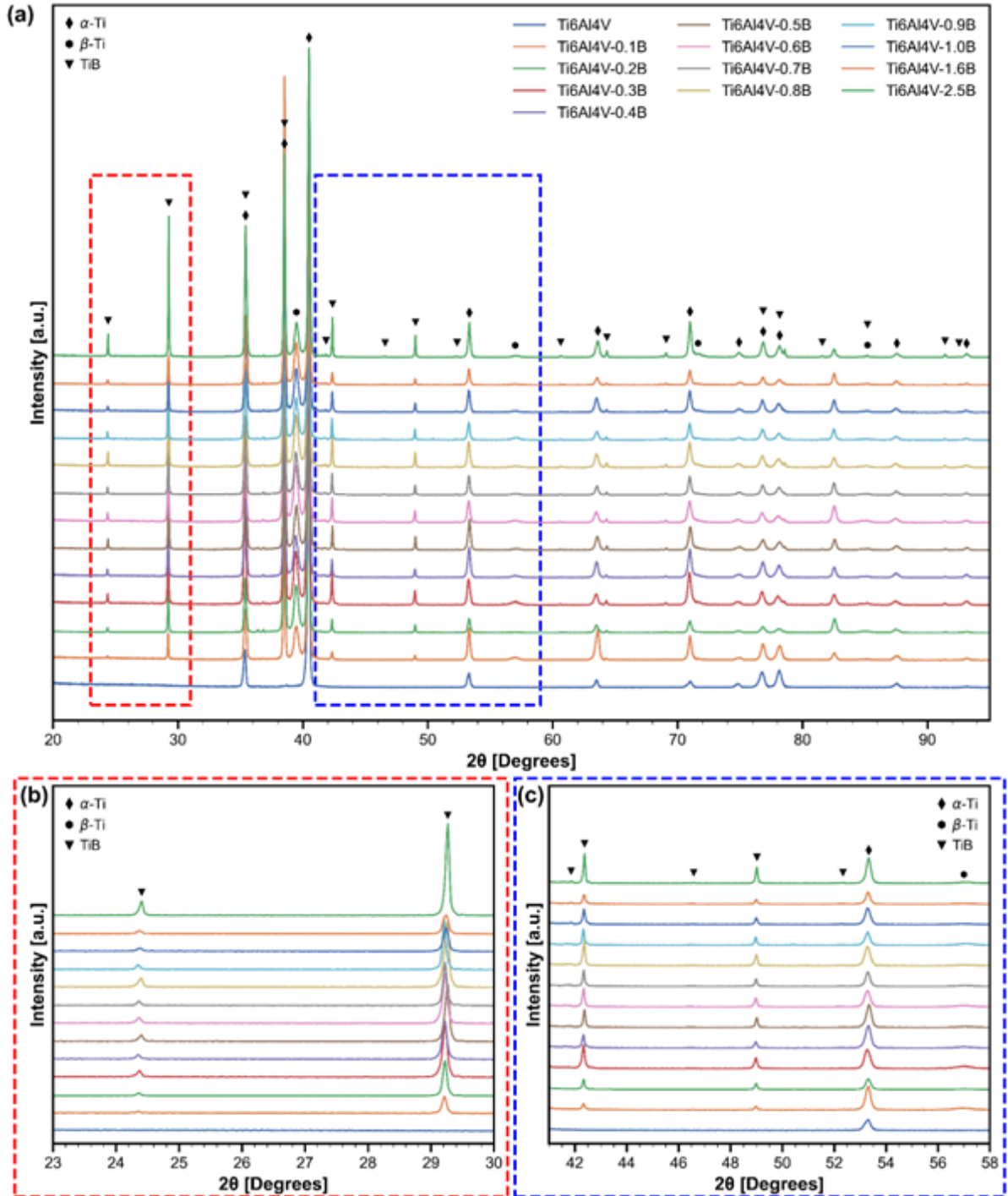


Figure 4-6 The characteristic XRD spectrum showing the consisting phases of arc melted Ti6Al4V-xB alloy buttons (a) over a wide range of $2\theta=20 - 95^\circ$; the enlarged view of XRD patterns within the 2θ ranges (b) $2\theta=23^\circ - 30^\circ$ and (c) $2\theta=41^\circ - 58^\circ$.

4.2.4 Reconstructed β Microstructure and Texture

Parent β -grain reconstruction process was carried out based on OM image and the EBSD results obtained from Ti6Al4V-xB alloy compositions on the XZ surface. The EBSD inverse pole figure orientation maps of the reconstructed prior- β grains in Ti6Al4V-xB alloys (Figure 4-7(a)-(f)) reveal significant changes in the prior β grain size with increasing boron content. The reconstructed β grains of the base Ti6Al4V alloy (Figure 4-7(a)) revealed relatively large with their thickness of approximately 1.5mm and homogeneously distributed grains having similar orientation, indicative of the baseline microstructure. With the addition of 0.1 wt.%B (Figure 4-7(b)), the reconstructed β microstructure showed a pronounced reduction in grain width, highlighting the initial grain refinement effect of boron. This trend of refinement continued with Ti6Al4V-0.5B alloy (Figure 4-7(c)), where the grains become noticeably less elongated and narrower. At 1.0 wt% B (Figure 4-7(d)), the grain structure transitioned to a more equiaxed morphology compared to the lower boron content samples, suggesting a significant alteration in the grain growth dynamics due to boron addition. With 1.6 wt.%B (Figure 4-7(e)), the grains maintained a fine, equiaxed structure as well as some elongated β -grains, indicating the grain refinement effect of boron was stabilized at this concentration. The most substantial grain refinement was observed in the Ti6Al4V-2.5B alloy (Figure 4-7(f)), where the grains are uniformly equiaxed and finely distributed across the microstructure. The scale bars in the images—1 mm for the OM image and 500 μm for the EBSD maps—clearly illustrate the dramatic reduction in grain size from the millimetre range in the base alloy to sub-millimetre ranges in the boron-added alloys.

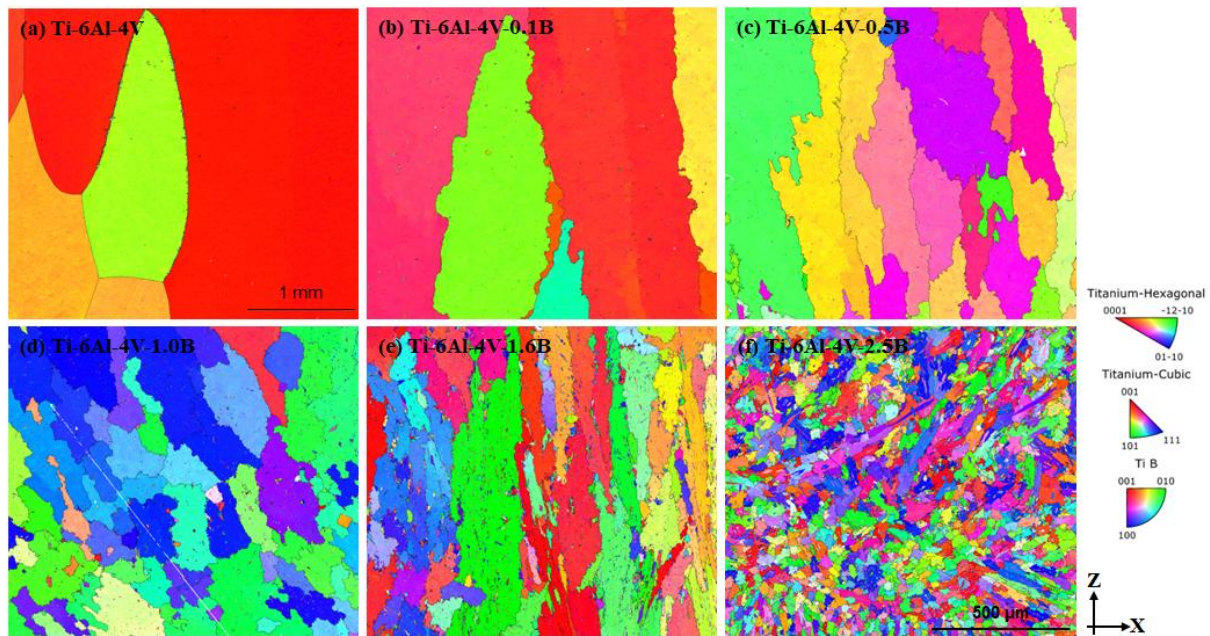


Figure 4-7 EBSD inverse pole figure orientation maps of reconstructed β phase in (a) Ti6Al4V, (b) Ti6Al4V-0.1B, (c) Ti6Al4V-0.5B, (d) Ti6Al4V-1.0B, (e) Ti6Al4V-1.6B and (f) Ti6Al4V-2.5B on XZ surfaces. Scale bar for the base alloy is 1 mm while it is 500 μm for boron modified counterparts.

Figure 4-8 demonstrates a clear and significant relationship between boron content and grain size in the examined alloy compositions. As the boron content increases, there is a notable decrease in grain size. While the prior- β grain size of the base alloy was observed to be approximately 1700 μm , almost an order of magnitude reduction in grain size to about 275 μm with 0.1 wt.%B addition was observed. As the boron content increased to 0.2 wt.%, the prior- β grain sizes further reduced to approximately 110 μm . However, further additions of boron did not lead to such marked variations, with grain size deducing by $\sim 10\%$ when the boron addition is increased from 0.2 to 0.3 wt.%. The prior- β grain sizes were stabilised around $\sim 60\mu\text{m}$ up to 2.5wt%B. This stabilization indicates a saturation point where additional boron does not significantly contribute to further grain size reduction. However, 2.5wt.%B addition caused further refinement in the alloy composition. The relationship between boron content and grain size (d_β) is well described by the exponential decay function:

$$d_\beta = 67.59 + 1632.01 \times \exp(-21.32 \times \text{wt.\%B}) \quad 4.6$$

Figure 4-8 also shows the variation of the volume fraction of α phase. It is seen that volume fraction of α phase increases from 86% in the base alloy to 89% in 0.1 wt.%B alloy. This is possibly due to α stabilizing effect of boron. However, as the boron content increases further beyond 0.1 wt.%, the volume fraction of the α phase begins to decrease gradually. By the time the boron content reaches 2.5 wt.%, the volume fraction of the α phase is reduced to around 77%. This trend indicates while small additions of boron can stabilize the α phase, higher concentrations of boron have the opposite effect, reducing the volume fraction of the α phase significantly. This reduction is due to the increased formation of TiB along the grain boundaries, occurring at the expense of the grain boundary α phase.

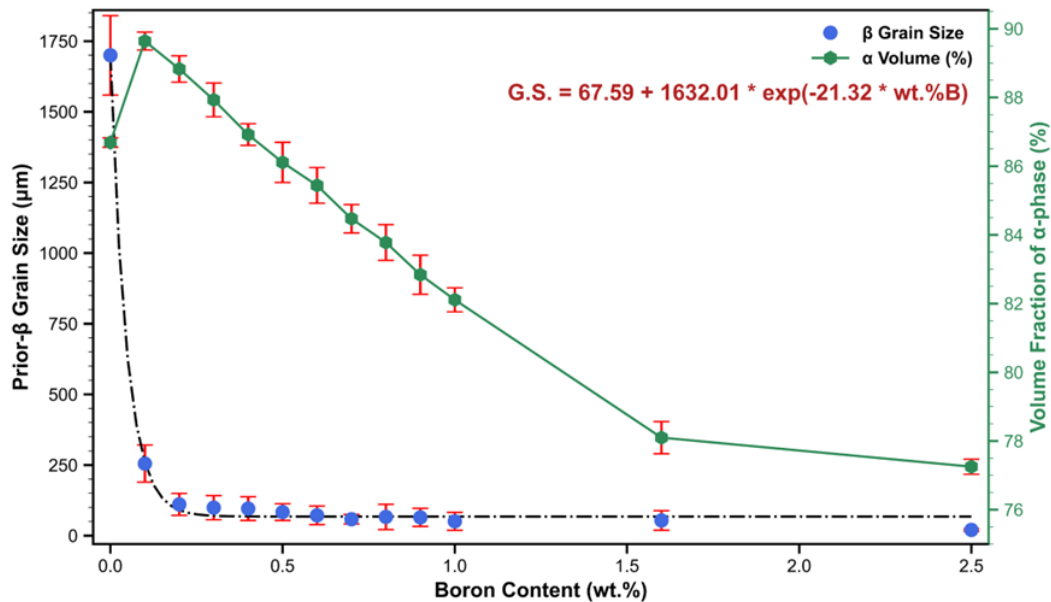


Figure 4-8 Variation of prior- β grain size and volume fraction of α -phase with wt.%B addition to Ti6Al4V-xB alloys.

Figure 4-9 presents the pole figures of the reconstructed β -grains for the Ti6Al4V-xB alloys with varying boron content, specifically (a) Ti6Al4V, (b) Ti6Al4V-0.1B, (c) Ti6Al4V-0.5B, (d) Ti6Al4V-1.0B, (e) Ti6Al4V-1.6B, and (f) Ti6Al4V-2.5B. The pole figures were aligned perpendicular to the longitudinal (Z) direction, corresponding to the cooling direction. These images provide a clear view of the crystallographic texture and the distribution of the β -grains. It is important to note, however, that the following observations are based on a limited and potentially uneven sampling region, which could influence the apparent texture intensities and might not fully represent orientation distribution of the entire sample. Despite these limitations, several notable trends emerged. In the base Ti6Al4V alloy, the local texture of the examined region was the highest, with the maximum texture intensity at 30.5 and texture index at 65.83 due to very large and oriented grains. In the Ti6Al4V-0.1B alloy (Figure 4-9(b)), the local texture of the examined region was still strong, with the maximum texture intensity at 27.2 and texture index at 59.4, but texture intensity and index were lower than that of the base alloy. With the addition of 0.5 wt.%B (Figure 4-9(c)), the maximum texture intensity and texture index decreased to 22.4 and 37.5, respectively, signifying a reduction in grain size and an increase in grain boundary area. As the boron content increases, the local texture of examined regions was decreased. While the texture intensity and texture index of Ti6Al4V-1.0B (Figure 4-9(d)) alloy was 13.9 and 14.09, respectively, texture intensity at 10.1 and texture index at 10.97 were measured for Ti6Al4V-1.6B (Figure 4-9(e)) alloys. These results indicated a more significant grain refinement and randomized texture. The most pronounced grain refinement is observed in the Ti6Al4V-2.5B alloy (Figure 4-9(f)), where the texture intensity and index values reached their lowest value of 1.9 and 1.4, respectively. This low texture index suggested a highly refined and randomized grain structure, demonstrating the substantial impact of higher boron content on the grain size and orientation.

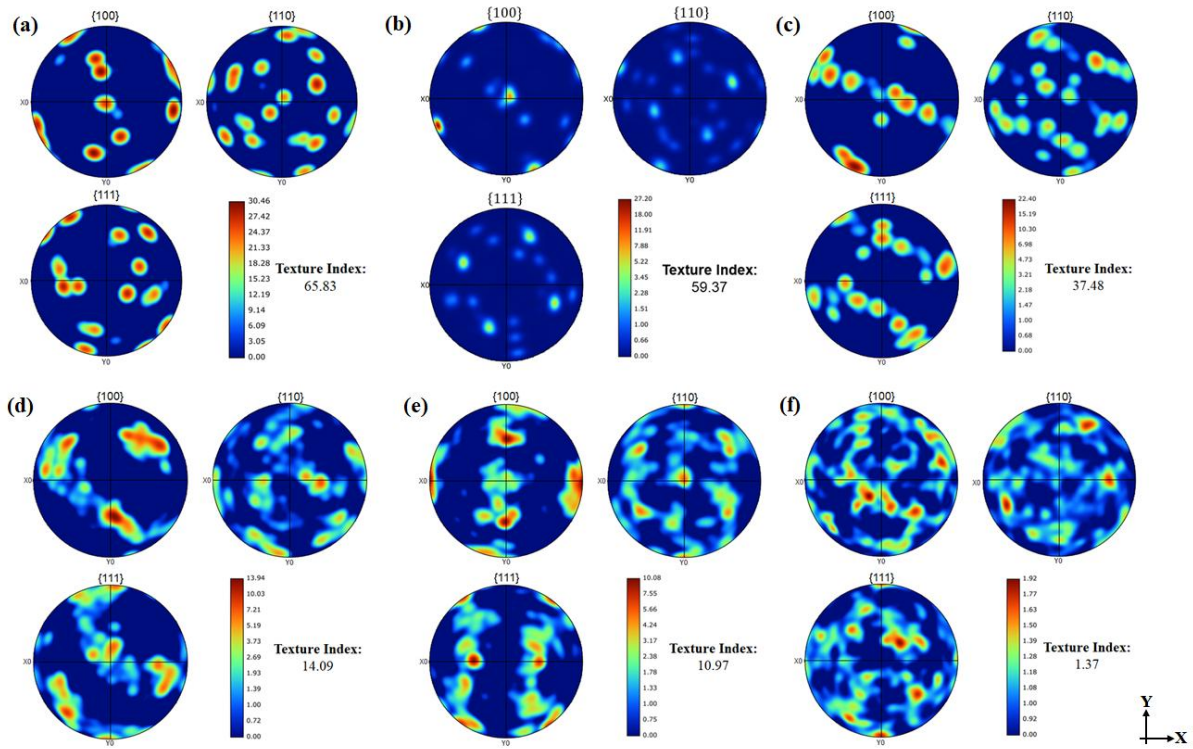


Figure 4-9 Pole figures of the reconstructed β -grains as revealed in Figure 4-7, with (a) Ti6Al4V, (b) Ti6Al4V-0.1B, (c) Ti6Al4V-0.5B, (d) Ti6Al4V-1.0B, (e) Ti6Al4V-1.6B and (f) Ti6Al4V-2.5B. The pole figures were rotated to be perpendicular with the longitudinal (Z) direction, which is the cooling direction.

In the pole figures with rotated coordinate, one of the $\langle 100 \rangle$ poles in the reconstructed β -grains in Ti6Al4V-0.1B was parallel to the longitudinal direction, while the others were perpendicular with the longitudinal direction with some minor inclination (Figure 4-9(b)). A relatively small fraction of the $\langle 100 \rangle$ poles in the reconstructed β -grains in Ti6Al4V-0.5B were nearly parallel with the longitudinal direction, while the inclination was considerably large (Figure 4-9(c)). Most of $\langle 100 \rangle$ poles had no specific orientation relationships with the longitudinal direction with large inclination in Ti6Al4V-1.0B (Figure 4-9(d)), while small fraction of the $\langle 100 \rangle$ poles in the β grains in Ti6Al4V-1.6B (Figure 4-9(e)) were nearly parallel with the longitudinal direction with greater inclination. The most substantial dispersion occurs in the Ti6Al4V-2.5B alloy (Figure 4-9(f)), where the $\langle 100 \rangle$ poles are highly randomized, indicating an almost complete loss of preferred crystallographic orientation. Overall, while the apparent trends in texture refinement and randomization with increasing boron content are supported by these data, caution must be exercised when interpreting the specific texture intensities. Poor sampling and limited coverage can lead to over- or underrepresentation of certain orientations. Ensuring more comprehensive sampling—through larger scanned areas, finer step sizes, or multiple measurements—would provide a clearer picture of the true texture evolution in Ti6Al4V-xB alloys. Nonetheless, these findings suggest that increasing boron content refines the β -grain

structure and diminishes strong crystallographic orientations, potentially benefiting mechanical isotropy.

4.2.5 α Microstructure and Texture

The EBSD inverse pole figure orientation maps of the α -laths in Ti6Al4V-xB alloys (Figure 4-10(a)-(f)) reveal significant changes in the α microstructure with increasing boron content. Boron significantly altered all variants of the α phases, including α_{GB} and intragranular α -lath. The presence of grain boundary α was eliminated through boron addition. Furthermore, the α phase morphologies were also altered significantly with the boron addition as revealed by the calculated α lath thickness and colony size (Figure 4-11). With the addition of boron, the average α lath thickness was reduced $\sim 15\%$ from $1.30\mu\text{m}$ in Ti6Al4V to $1.1\mu\text{m}$ in Ti6Al4V-0.1B (Figure 4-11(a)). With higher addition of boron, the average α lath thickness was further reduced to approximately $0.72\mu\text{m}$ in Ti6Al4V-1.0B and $0.62\mu\text{m}$ in Ti6Al4V-2.5B (Figure 4-11(a)). The α -lath tends to be more equiaxed due to the boron addition, which can be revealed by the change of the aspect ratio (length/width). With only 0.1 wt.%B addition, the average α -lath aspect ratio reduced to 3.08. With more boron addition, the average α -lath aspect ratio reduced further to 1.77 (2.5 wt.%B addition).

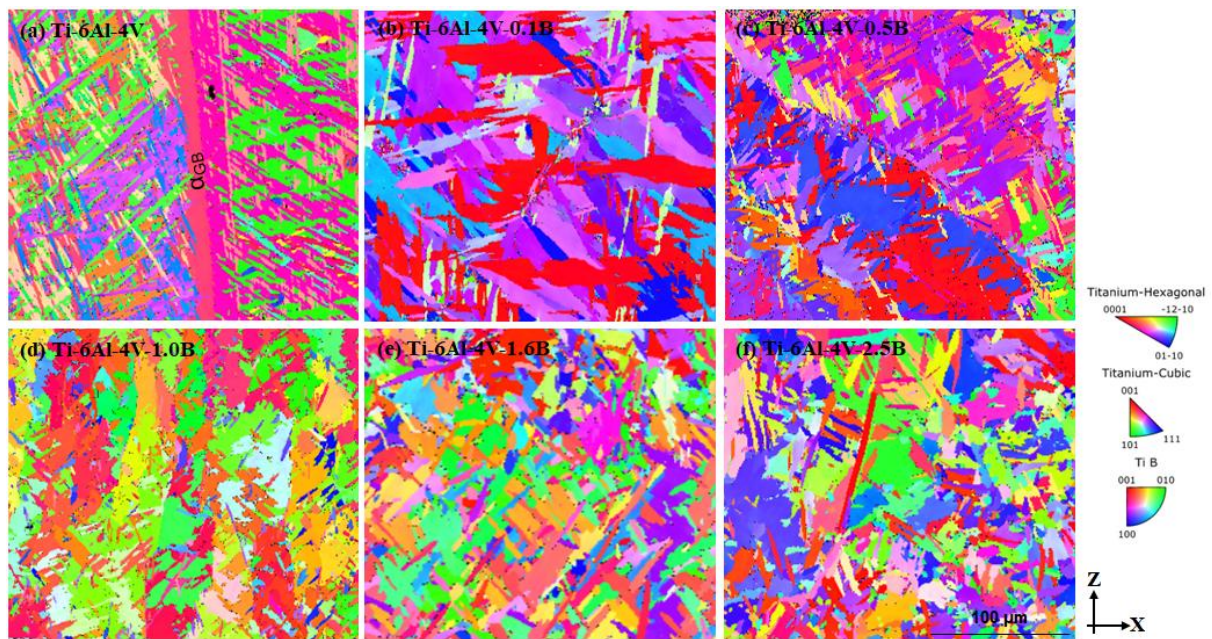


Figure 4-10 EBSD inverse pole figure orientation maps of the α phase in (a) Ti6Al4V, (b) Ti6Al4V-0.1B, (c) Ti6Al4V-0.5B, (d) Ti6Al4V-1.0B, (e) Ti6Al4V-1.6B and (f) Ti6Al4V-2.5B on XZ surfaces.

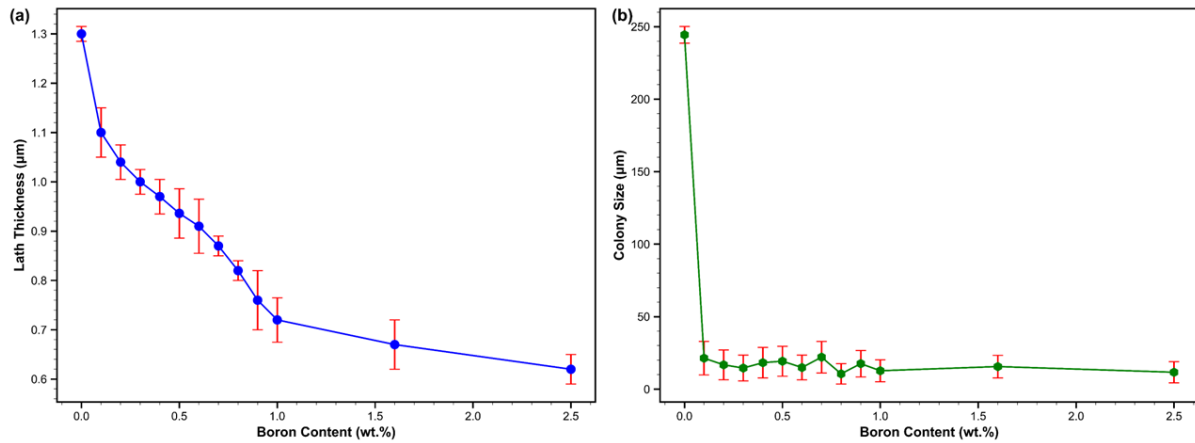


Figure 4-11 Variations of average (a) α lath thickness and (b) α colony size calculated from the SEM-BSE images taken from Ti6Al4V-xB alloy compositions.

In addition to prior β -grain texture, boron addition was also effective in eliminating the sharp α texture and reducing the texture intensities of the α phase in Ti6Al4V (Figure 4-12). For easy interpretation of the α texture in different Ti6Al4V with regards to the cooling direction, only the α texture on XY surfaces were used. The α texture on XY surfaces was representative of the α texture on the other surfaces. The base alloy (Figure 4-12(a)) showed texture index at 15.5 and texture intensity at 23.5. The α texture in Ti6Al4V-0.1B was very sharp, with the texture index of the examined area as 14.4 and the maximum texture intensity as 18.5 (Figure 4-12(b)). Since the examined area only contain a few prior- β grains and the α laths could be transformed from the same prior- β grain as indicated by the pole figures, the α texture of the examined areas could be considerably sharper than that in the bulk sample. The α texture was still sharp in Ti6Al4V-0.5B, while its intensity was reduced significantly in comparison with that in Ti6Al4V-0.1B, with the texture index reduced to 8.6 and the maximum texture intensity reduced to 10.1 on the examined area (Figure 4-12(c)). With boron addition of 1.0 wt%, the texture sharpness was further reduced. The texture index of Ti6Al4V-1.0B was only 4.0, with the maximum texture intensity 7.9 on the examined area (Figure 4-12(d)). The texture index and intensity were slightly increased to 4.2 and 10.7, respectively with the addition of 1.6 wt.%B (Figure 4-12(e)). The most pronounced grain refinement is observed in the Ti6Al4V-2.5B alloy (Figure 4-12(f)), where texture index and intensity reached to their lowest value of 1.2 and 2.1, respectively.

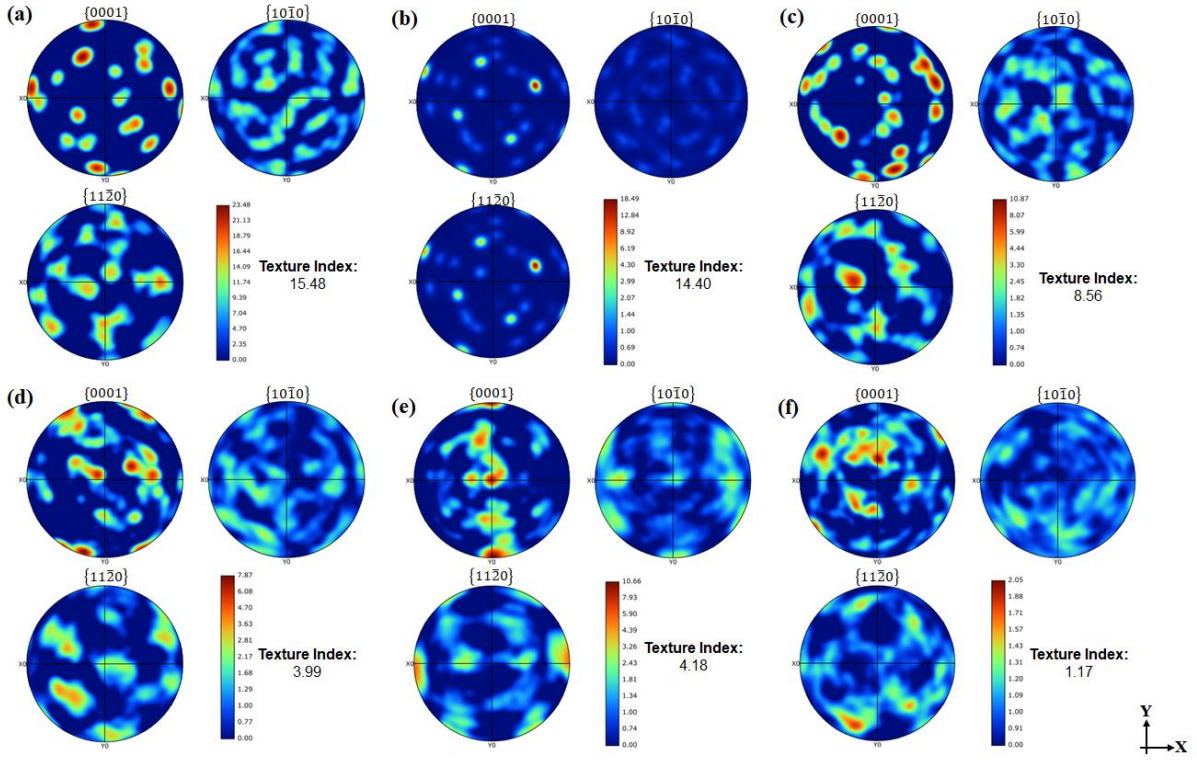


Figure 4-12 Pole figures and texture index of α phase in (a)Ti6Al4V, (b) Ti6Al4V-0.1B, (c) Ti6Al4V-0.5B, (d) Ti6Al4V-1.0B, (e) Ti6Al4V-1.6B and (f) Ti6Al4V-2.5B perpendicular with the longitudinal (Z) direction.

4.2.6 Characterization of TiB Phase in Ti6Al4V-xB Alloys

The investigation into the Ti6Al4V-xB alloys revealed key insights into the behaviour of the TiB phase with varying boron content, as presented in Figure 4-13. Figure 4-13(a) shows the variation in the volume fraction of TiB as a function of boron content. The experimentally measured volume fraction showed approximate linear relation with the weight percentage of boron. This trend is consistent with the computed volume fraction values, depicted by the dashed line, which was made assuming all the boron reacts with titanium to in-situ form TiB and the principles of mass conservation. The close alignment between the experimental data and theoretical predictions confirmed the reliability of the mass conservation model in predicting TiB volume fractions in these alloys. The good correlation observed between the experimental and predicted V_{TiB} values allows for the direct conversion of wt.% B added into V_{TiB} through the equation:

$$V_{TiB} = 5.23 \times wt.\%B \quad 4.7$$

As the boron content increases, the morphology of TiB precipitate underwent significant changes, as illustrated by the variation in aspect ratio data in Figure 4-13(b). Initially, with lower boron contents up to 0.4 wt.% B, TiB precipitates exhibited high aspect ratios, indicating

elongated, needle-like structures. With the addition of 0.5 wt.%B, TiB morphology began to diversify. In addition to the needle-like precipitates observed at lower boron contents, there was a notable presence of rod-like TiB precipitates. As the boron content reached 1 wt.%, the TiB particles transitioned to short, straight needle shapes or rod shapes. The aspect ratio decreased significantly, reflecting the formation of more rod-like TiB precipitates. With further increases in boron content, the morphology shifted to highly-faceted TiB rods shown in Figure 4-1. The quantity of these blocky particles was significantly higher in the 2.5B alloy compared to the 1.6B alloy. Notably, the aspect ratio of the TiB rods in the 2.5B alloy was about half that of the rods in the 1.6B alloy, indicating a significant change towards more rods-like precipitates.

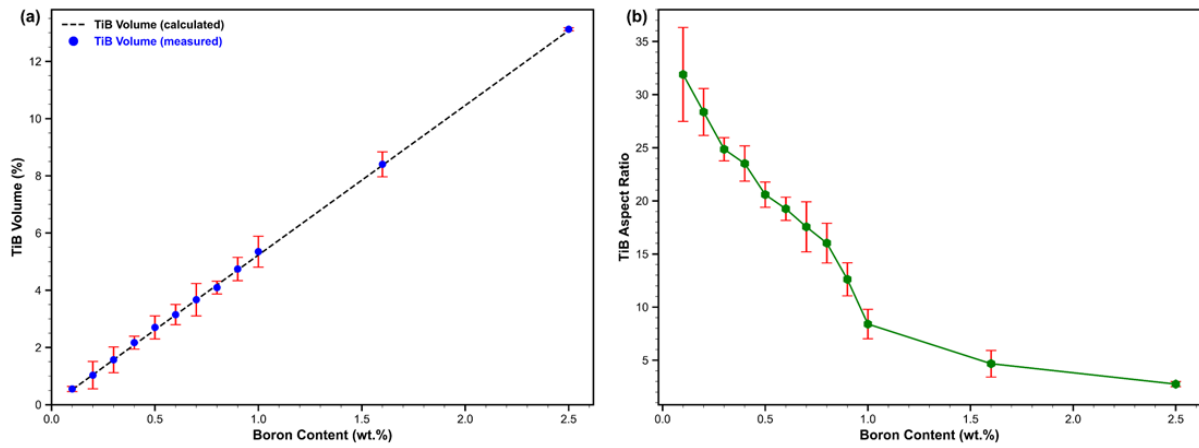


Figure 4-13 Variation of (a) experimentally measured volume fraction of TiB, V_{TiB} , as a function of boron contents in Ti6Al4V-xB alloys, where dashed line represents V_{TiB} computed using principles of mass conservation; (b) aspect ratio of TiB needles with increasing wt.%B.

4.3 Laser Glazed Ti6Al4V-xB: Effect of Boron Concentration

4.3.1 Hardness and Melt Pool Variation

To comprehend how boron content affects the hardness of laser glazed Ti6Al4V-xB alloys, nanoindentation tests were performed on laser remelted regions of all samples, as illustrated in Figure 4-14. Nanohardness measurements were conducted on five different melt pools, with each pool subjected to 10 indents. The nanohardness (H_d) is determined as the ratio of the peak indentation load (P_{max}) to the projected area of the indentation (A_c). The H_d value can be derived using the following equations (Attar et al., 2017):

$$H_d = \frac{P_{max}}{A_c} \quad 4.8$$

$$A_c = f(h_c^2) = 24.5h_c^2 \quad 4.9$$

where h_c represents the depth of contact at the maximum applied load. Figure 4-14(a) displays the nanoindentation load – penetration depth curves for the polished cross-sections of Ti6Al4V-

xB parts. It is evident that as the boron addition increases from 0 wt.% to 2.5 wt.%, the indentation depth correspondingly decreases from 1322nm to 1098nm. Conversely, as illustrated in Figure 4-14(b), the average values of nanohardness and Reduced modulus increase as the indentation depth decreases. The average nanohardness of alloy compositions were found to increase linearly with the boron concentration from approximately 3.65GPa (base alloy) to approximately 6.82GPa for 2.5 wt.% boron modified alloy. Similarly, average Reduced modulus values showed linear increment with added boron from approximately 99GPa (base alloy) to approximately 138GPa for 2.5 wt.%B alloy. Clearly, the hardness increases progressively with the addition of boron. This enhanced surface hardness is attributed to the hardening effect of the high-hardness nanoscale needle-like TiB ceramic. While the estimated hardness for the composite material reaches approximately 5.72GPa at 13 vol% TiB based on the rule of mixtures, the measured average nanohardness value for the Ti6Al4V-2.5B alloy was significantly higher at 6.82 GPa. This suggests that, in addition to the reinforcement effect of TiB particles, there must be a considerable contribution from grain refinement. The addition of boron likely leads to a refinement of the laser-glazed microstructure, further enhancing the hardness of the alloy beyond what is predicted by the rule of mixtures alone.

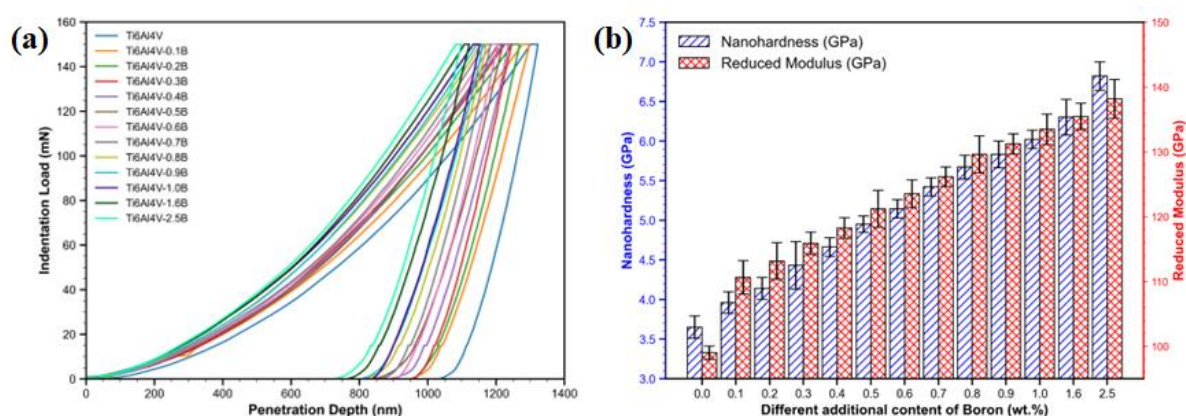


Figure 4-14 (a) load-penetration depth curves; (b) calculated nanohardness (H_d) and Reduced modulus (E_r) values of samples with different boron concentrations.

Figure 4-15 illustrates the variation in melt pool depths as a function of boron concentration. Similar to the average nanohardness values, the melt pool depth significantly increases with the addition of boron. There is a strong linear relationship between the measured melt pool depth and boron concentration in Ti6Al4V-xB alloys. When boron content surpasses the maximum solubility in the α -titanium phase during cooling, the TiB phase is in-situ formed through an exothermic reaction. This formation releases 2.99 kJ/g of energy (H. Li et al., 2020). Consequently, it is believed this exothermic reaction could extend the life of the melt pool, thereby increasing the depth and width of the observed track cross-sections.

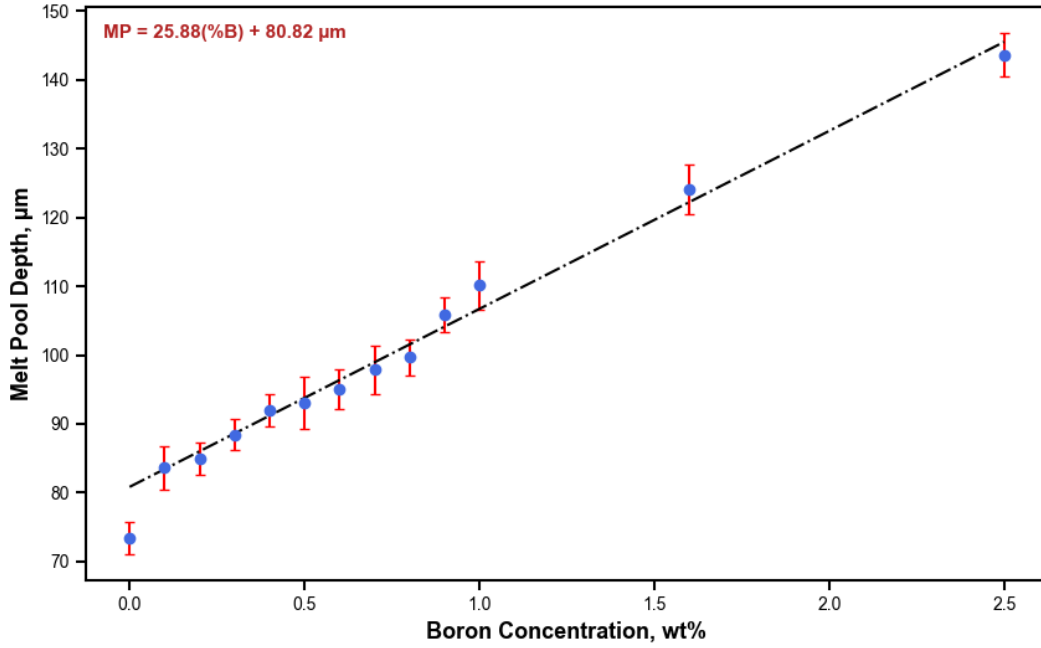


Figure 4-15 Melt pool depth as a function of boron concentration in laser surface glazed Ti6Al4V-xB alloys prepared by arc melting.

4.3.2 Phase Identification and Analysis

The XRD patterns displayed in Figure 4-16 illustrate the phases present in surface laser glazed Ti6Al4V-xB alloy buttons. The predominant phase detected is either α -titanium or α' martensite. Additionally, some TiB peaks overlap with the martensite α' -titanium peaks, making them difficult to distinguish within the pattern. It is also noteworthy that the addition of boron results in a noticeable broadening of the peaks in the spectra. This is reflected in the full width at half maximum (FWHM) values, which increased from 0.597 for the base alloy to 1.178 for the Ti6Al4V-2.5B alloy at high angle peaks. The alteration in the half-peak width can be explained using the Scherrer equation (A. S. Patil et al., 2019):

$$\beta_s(2\theta)_{hkl} = \frac{\kappa\lambda}{T \cos \theta_{hkl}} \quad 4.10$$

where β_s denotes the grain size contribution to the peak width at half maximum, κ is a constant, λ represents the X-ray wavelength, θ is the diffraction angle, and T signifies the average grain thickness perpendicular to diffraction plane. During the XRD analysis of Ti6Al4V-xB alloy samples, it was found that increasing the boron concentrations led to a reduction in crystallite size, as evidenced by the broadening of the XRD peaks at half maximum. This empirical data indicates a consistent decrease in crystallite size with higher boron levels in the alloys. Additionally, samples with elevated boron concentrations showed more significant peak broadening, reflecting lattice distortion within the alloy matrix and correlating with the increased presence of TiB structures.

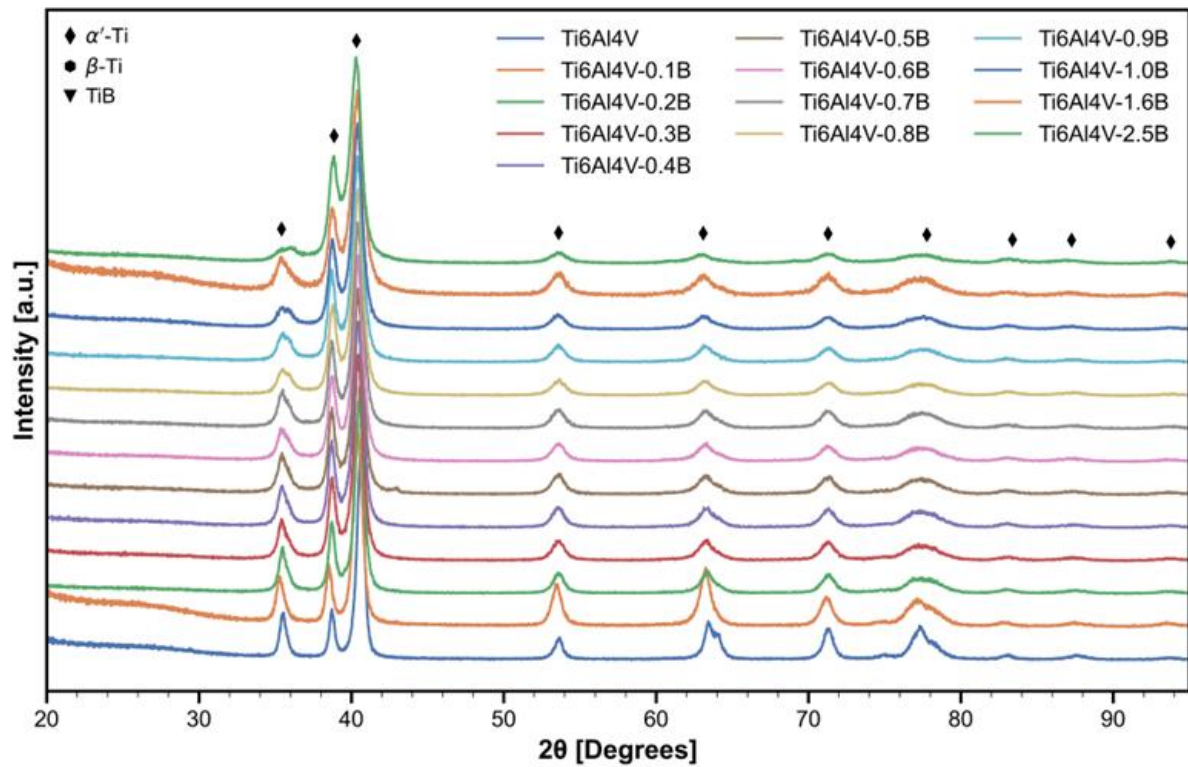


Figure 4-16 XRD spectrum displaying the phases present in surface laser-glazed Ti6Al4V-xB alloys, fabricated using arc melting.

Figure 4-17 illustrates the 2θ peak position of the predominant α' -titanium phase in relation to B concentration. The figure shows that the main α'/α -titanium peak moves to the left, indicating a reduction in the 2θ angle. The martensitic transformation temperature decreases as the boron concentration increases, facilitating the transformation from $\beta \rightarrow \alpha$ -titanium (Cai et al., 2019; M. Fang et al., 2021; W. J. Lu et al., 2008). This shift in the 2θ peaks to lower angles in the surface laser glazed samples suggests the presence of an α/α' phase mixture. Moreover, the XRD patterns indicated significant differences in the lattice parameters of Ti6Al4V-xB alloys compared to the base Ti6Al4V alloy, pointing to localized lattice distortions caused by the in-situ formation of TiB structures. The volume fraction of TiB structures within the matrix appeared to affect the overall lattice parameters of the alloy, creating stress fields that influenced the lattice spacing in the surrounding matrix. This was evidenced by a shift to lower 2θ values in the XRD patterns, signifying lattice expansion due to TiB formation.

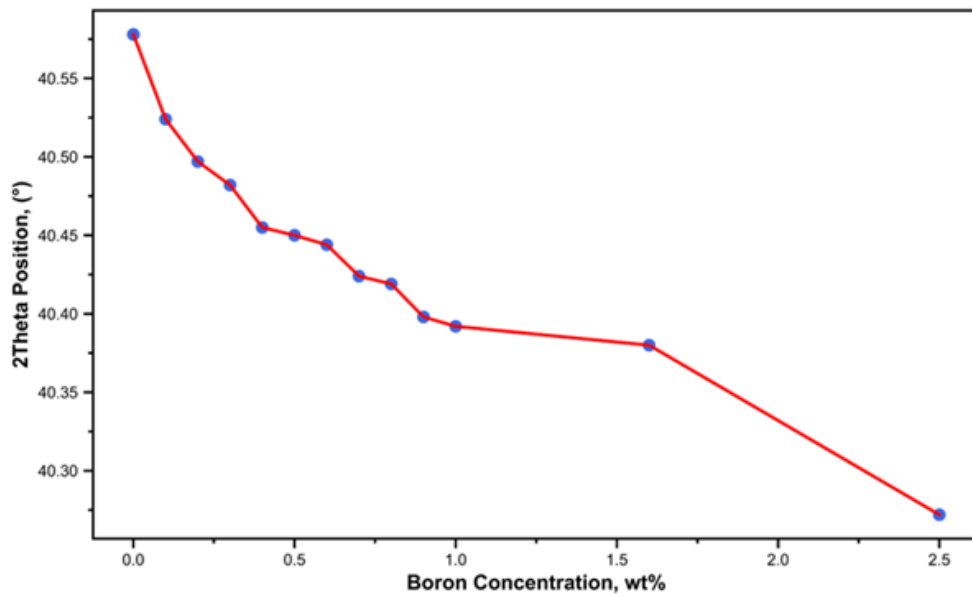


Figure 4-17 The relationship between the boron concentration and the 2θ peak position of the most prominent α' -titanium phase.

4.3.3 Microstructural Analysis

Figure 4-18 illustrates the development of microstructural morphologies in surface laser glazed Ti6Al4V-xB alloy samples. The microstructure of the Ti6Al4V alloy primarily consists of acicular α' -titanium (Figure 4-18(a)). When a trace amount of boron (0.1 wt.%) is added, the microstructure remains largely unchanged, with acicular α' martensite still present (Figure 4-18(b)). However, this small addition of boron reduces the width and length of the martensitic α' laths. As shown in Figure 4-18(c), increasing the boron content to 0.2 wt.% introduces a second phase supposed to be TiB, which appears as a fuzzy, discontinuous structure alongside the acicular α' martensite. This structure becomes quasi-continuous with higher boron concentrations, as depicted in Figure 4-18(e) – (f). At boron concentration of approximately 0.6 wt.%, a fully continuous distribution of the second phase is observed, as seen in Figure 4-18(g) – (m). Moreover, Figure 4-18(d) indicates that in alloys with 0.3 wt.%B or more, the α' phase is no longer visible, and the microstructure appears to fully develop into an $\alpha+\beta$ structure.

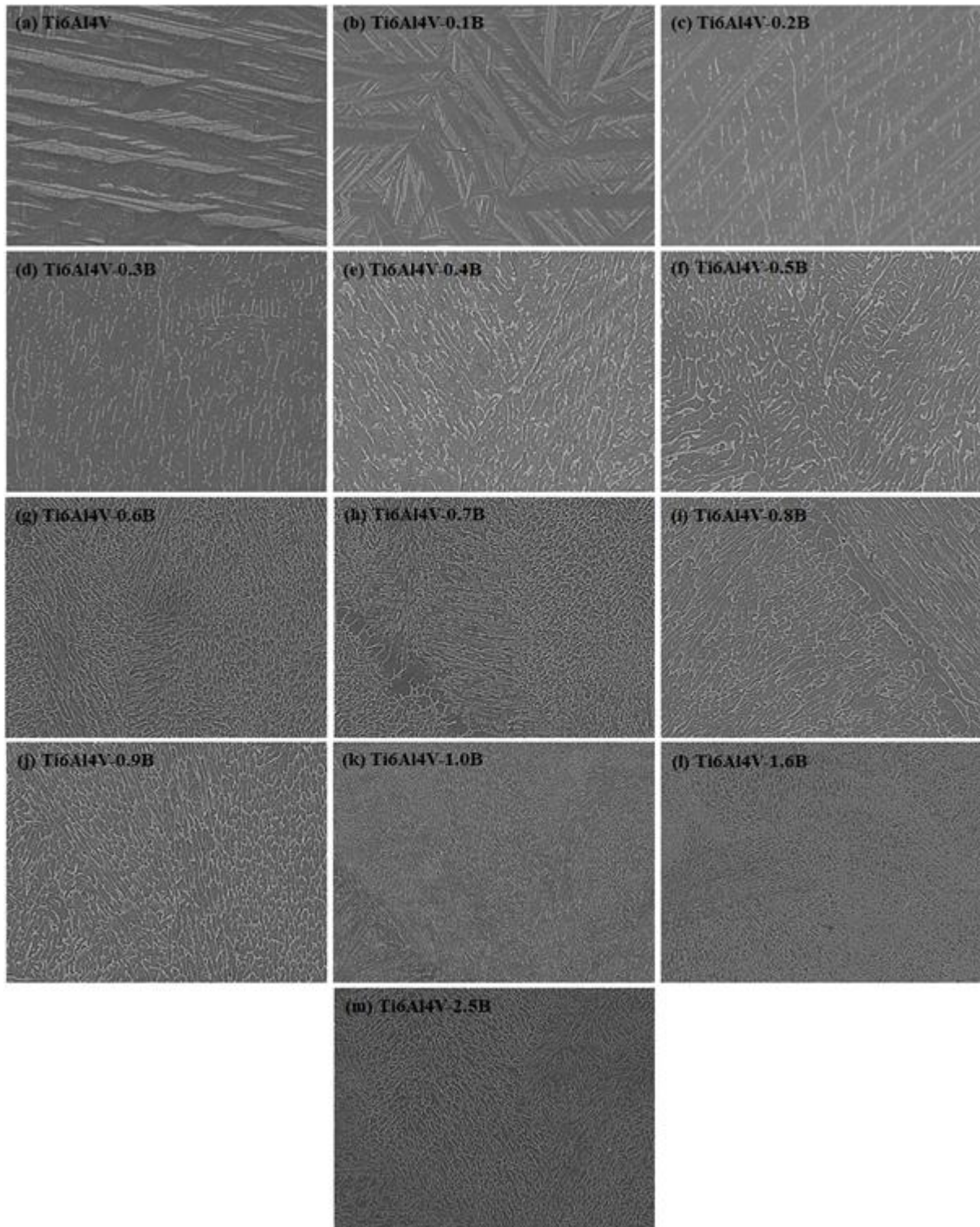


Figure 4-18 SEM-SE images depicting the microstructure of laser-glazed Ti6Al4V-xB, processed with 13 varying concentrations of boron.

TEM analysis was employed to characterize the microstructural features of the base alloy and the inter-lath bright phase observed in Figure 4-18(c) – (m). Figure 4-19(a) displays a SEM-SE

image of the Ti6Al4V alloy. The highlighted rectangle indicates the area from which the TEM foil was extracted. Figure 4-19(b) demonstrates that martensitic α' -titanium is the predominant phase in the sample. Figure 4-19(c) - (d) illustrate that the prevalent α' martensite within the microstructure measures approximately 200 nm in thickness and exhibits a high dislocation density. Figure 4-19(e) – (h) present selected area electron diffraction (SAED) patterns captured from the titanium matrix (e) and within the individual α' -titanium lath (g). The SAED patterns from the titanium matrix confirm the absence of other phases, such as β -titanium, while those from the individual lath confirm an HCP structure, verifying the martensitic α' nature.

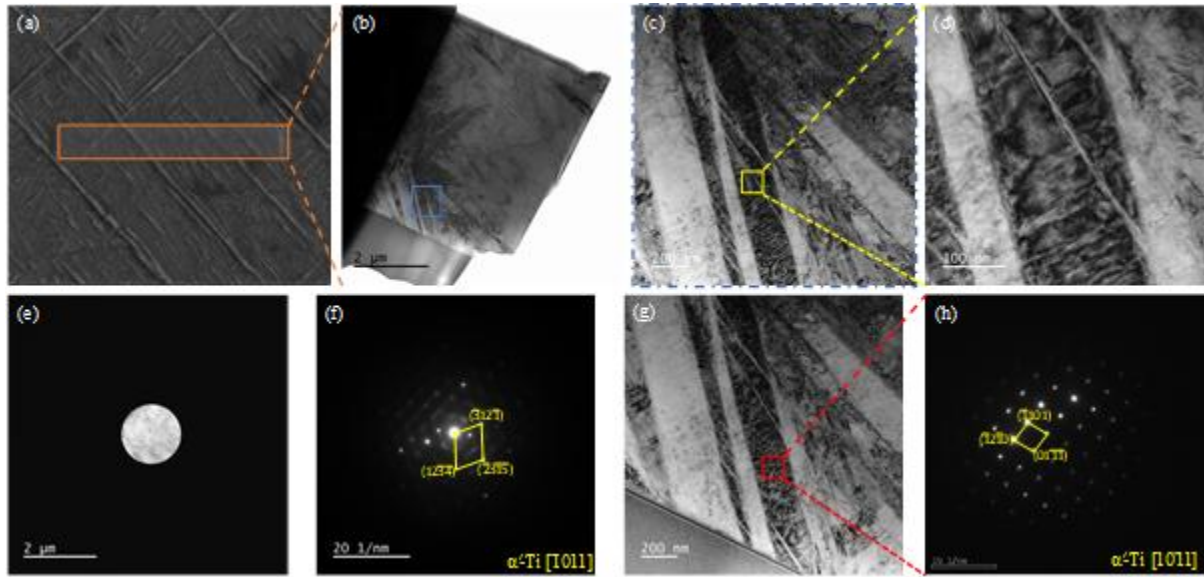


Figure 4-19 SEM and TEM micrographs of the laser-glazed surface of the base Ti6Al4V alloy: (a) Secondary electron image depicting the titanium matrix; (b) Bright-field image of the TEM foil illustrating α' martensite; (c) Bright-field morphology showcasing the α' martensite; (d) Higher magnification bright-field image of the α' -martensite; (e) TEM aperture size highlighting the region of interest; (f) The corresponding selected area electron diffraction (SAED) pattern of the region of interest; (g) Bright-field image revealing α' -titanium; (h) Corresponding SAED pattern of the specified region.

Figure 4-20(a) presents SEM-BSE image of the Ti6Al4V-1.0B alloy composition, which was used to prepare the TEM foil. The TEM bright-field micrograph shown in Figure 6 (b) demonstrates the predominant phase in the specimen is α' martensitic. TiB structures are clearly visible, adorning the α' grain boundaries. Figure 4-20(c) and (d) illustrate that the primary α' martensite appears as fine needle-like structures, suggesting that the growth of α' martensite is hindered by the presence of in-situ formed TiB structures. The TiB crystallographic structure in titanium matrix composites, known as the B27 structure, has been documented by Lu et al. (D. He et al., 2023; C. Liu et al., 2023). TiB with the B27 structure exhibited preferential growth along the [010] direction, leading to a needle-like morphology with a hexagonal cross-section (Rahman Rashid et al., 2018; Tichelaar et al., 2020). Figure 4-20(b) and (e) display bright-field images of TiB structures in a cellular-type formation, indicating that nanoscale TiB structures were formed in-situ in the titanium matrix following laser surface glazing. High-resolution

TEM (HRTEM) images of TiB structures and their corresponding fast Fourier transform (FFT) profile in region A (Figure 4-20(g)) in Figure 4-20(f) confirm the presence of the B27 structure of TiB. Thus, the TiB structures in this study are inferred to possess the stable B27 orthorhombic structure, characterized by needle-like morphology. It is also observed that a high density of faults is present within these reinforcements as shown in Figure 4-20(i). Furthermore, due to the thermal expansion mismatch between ceramic reinforcements and the titanium matrix, dislocations are observed around TiB structures in the matrix (Y. He et al., 2019; Khairallah et al., 2016; Tao, Yao, & Zhang, 2018). HRTEM analysis was also conducted on the reinforcement-matrix interface of the in-situ synthesized TiB structures, revealing a clean interface between the TiB structure and α' -Titanium, indicating strong interfacial bonding at the atomic scale as seen in Figure 4-20(h). Given titanium's α phase has ultra-low solid solubility for B, there is minimal likelihood for B composition gradients along the precipitates. The significant streaking in the SAED patterns in Figure 4-20(j) and (k) is due to numerous stacking faults within the TiB (B27) structure along the (011) direction. Notably, Thon rings, observed in Figure 4-20(g), (j), and (k), are a characteristic phenomenon in the power spectra of bright-field (BF) TEM micrographs (Stjohn et al., 2011). These rings result from the contrast transfer function, which modulates the Fourier transform of the object based on defocus variations.

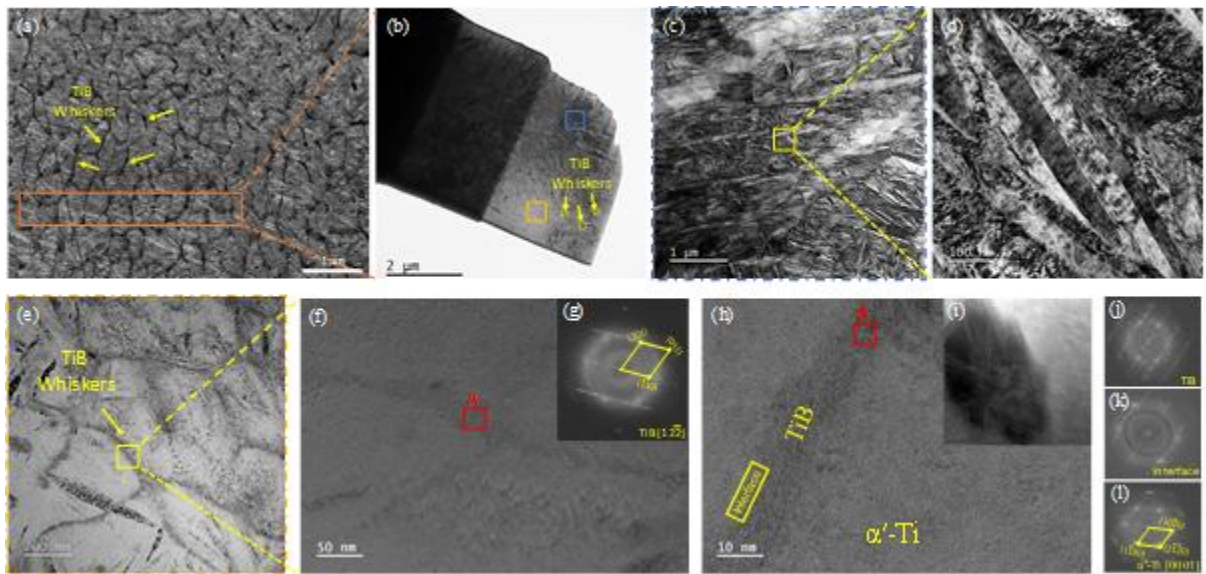


Figure 4-20 SEM and TEM micrographs of the laser surface glazed Ti6Al4V-1.0B alloy reveal the following: (a) A backscattered electron image displaying the TiB structures within the titanium matrix, (b) A bright-field TEM foil image highlighting α' martensite and a cellular-typed TiB structure, (c) The bright-field morphology of the α' martensite, (d) A higher magnification bright-field image of α' -martensite, (e) The bright-field morphology of the TiB structure, (f) An HRTEM image, (g) The corresponding FFT profile in region A (inset) of the TiB structure, (h) An HRTEM image of a pristine α' -Titanium/TiB interface, (i) Region B (inset) depicting highly faulted TiB, and the FFT profiles of the TiB phase (j), interface (k), and α' -titanium phase (l).

Figure 4-21 illustrates the elemental distribution of the Ti6Al4V-1.0B alloy as analysed using TEM electron-dispersive spectroscopy (EDS) and electron energy loss spectrometry (EELS). The EDS elemental mapping of a selected region reveals a uniform distribution of Ti (Figure 4-21(c)) and V (Figure 4-21(e)) within the matrix. In contrast, the alloying element Al (Figure 4-21(d)) displays distinct partitioning behaviours within the titanium matrix. The EDS mapping highlights a microstructure primarily composed of martensitic α' titanium and titanium boride (TiB) phases, with a notable absence of the β -titanium phase. Figure 4-21(f) demonstrates that boron forms a quasi-continuous network. A comparison between Figure 4-21(e) and Figure 4-21(f) shows that Boron-enriched regions are depleted of Al while maintaining a similar Ti content as the matrix. EELS analysis, conducted in the selected region for enhanced signal-to-noise ratio and higher spatial resolution of light elements, is depicted in Figure 4-21(h). Figure 4-21(i) – (l) display the EELS spectra for elemental distributions, an FFT image of background-subtracted EELS spectra, and the elemental distribution of B and Ti, respectively. The EELS elemental mapping reveals a homogeneous distribution of Ti within the matrix (Figure 4-21(k)) and B-enriched areas (Figure 4-21(l)), corroborating the results observed in the TEM EDS mapping. These elemental maps confirm the presence of in-situ synthesized TiB in the Ti6Al4V-xB alloy compositions, identified as the white-contrast phase in SEM secondary electron images of Ti6Al4V-xB alloy compositions.

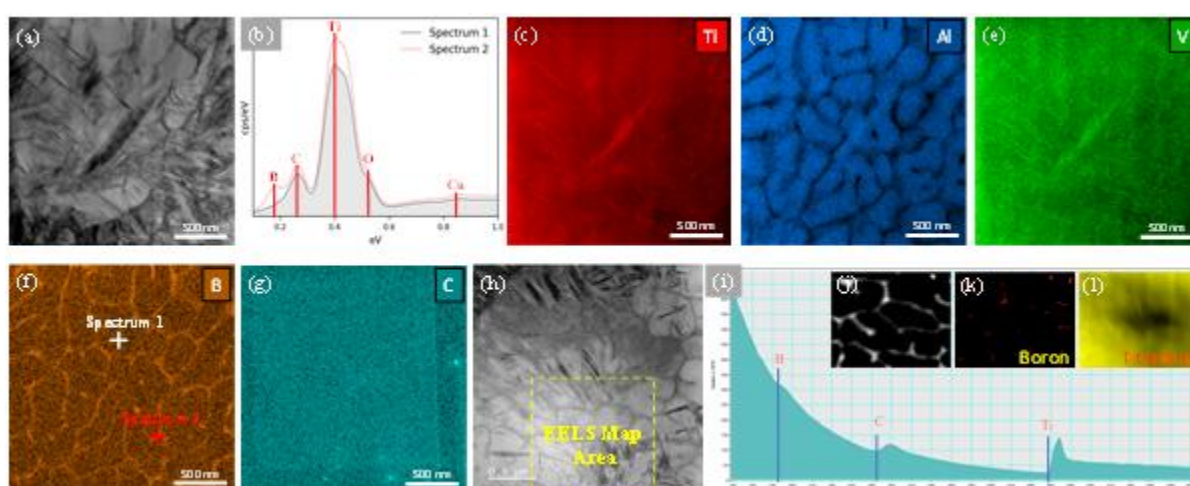


Figure 4-21 Elemental distribution in laser surface glazed Ti6Al4V-1.0B alloy via TEM-EDS and EELS analysis: (a) TEM bright-field image displaying the EDS map of the chosen area; (b) EDS spectrum for the identified regions; EDS mapping for the bright-field image illustrating the distribution of elements: (c) Ti, (d) V, (e) Al, (f) B, and (g) C; (h) TEM bright-field image presenting the EELS map of the selected area; (i) EELS mapping for the bright-field image depicting (j) integrated signal over the zero-loss peak and B peak, and the corresponding distributions of (k) B and (l) Ti.

4.3.4 Reconstructed Prior- β Microstructure

Figure 4-22 illustrates the reconstructed prior β -grains in the surface laser glazed Ti6Al4V-xB alloy compositions. Electron backscatter diffraction analysis reveals that the Ti6Al4V alloy

features large columnar prior β -titanium grains. Micrographs show that increasing the boron concentration in the surface laser glazed alloy compositions leads to a significant reduction in grain size. When the base alloy undergoes surface laser glazing, a minimal reduction in the average grain size is observed, implying that the original grains are epitaxially grown from the prior β -grains. Introducing a nominal 0.1 wt.%B modification results in a noticeable decrease in grain size, highlighting the impact of boron addition on grain refinement. Further increasing the boron concentration to 0.2 wt.% continues to reduce the grain size, suggesting potential for ongoing grain refinement with higher boron contents. With boron concentrations up to 2.5 wt.%, the alloy compositions experience significant grain refinement, resulting in a microstructure comprising near-equiaxed and/or equiaxed prior β -grains. These findings indicate that as the boron concentration increases, the number of in-situ synthesized TiB, which serve as heterogeneous nucleation sites, also increases, making in-situ grain refinement evident as shown in Figure 4-22.

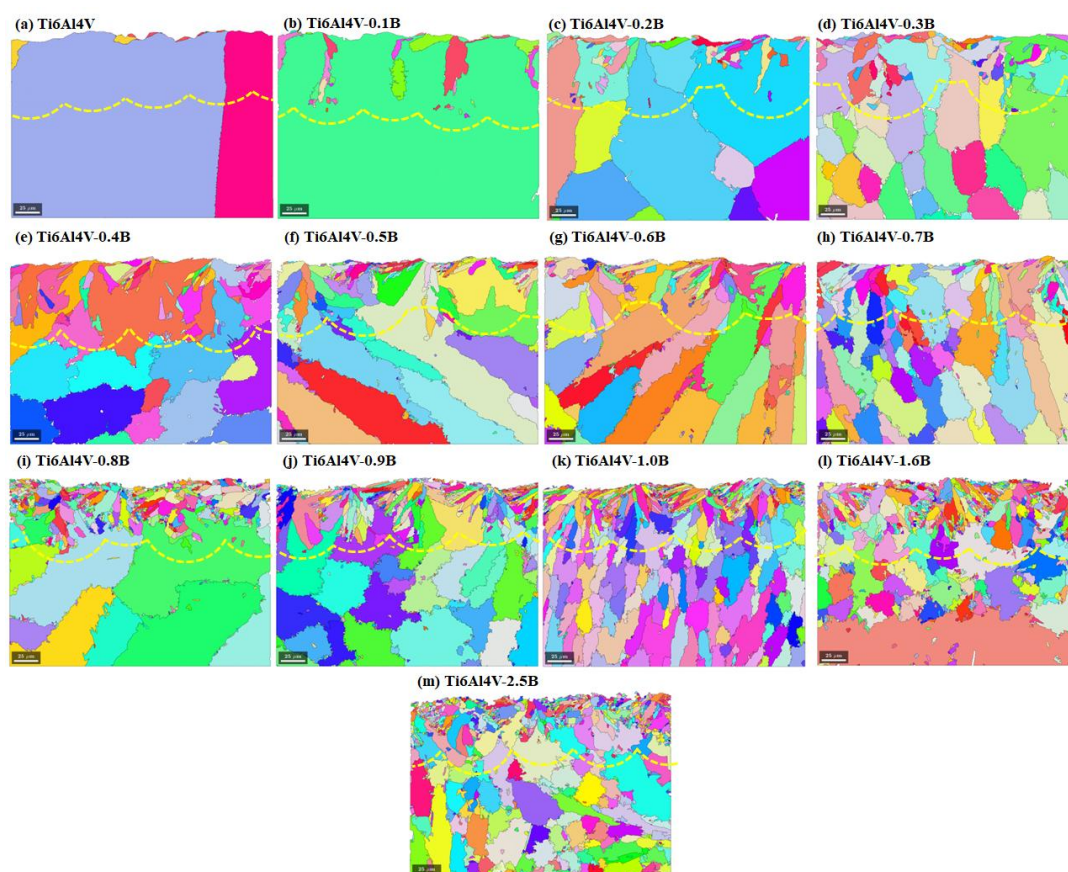


Figure 4-22 Reconstructed prior β -grain sizes of surface laser-glazed Ti6Al4V-xB alloy compositions. The yellow dashed line marks the melt pools created by the laser glazing process.

Figure 4-23 presents the average measurements for the length, width, and aspect ratio of the α -laths in surface laser glazed Ti6Al4V-xB alloy compositions. As the boron concentration increases, there is a significant reduction in the lengths and aspect ratios of α -laths,

accompanied by a notable increase in their widths. 0.1 wt.%B addition leads to an approximate 8% reduction in length and a 13% reduction in aspect ratio of the α -laths compared to those in the Ti6Al4V alloy. With further boron addition, these reductions become even more pronounced. The changes in α -lath size result from the combined influences of grain refinement and cooling rate.

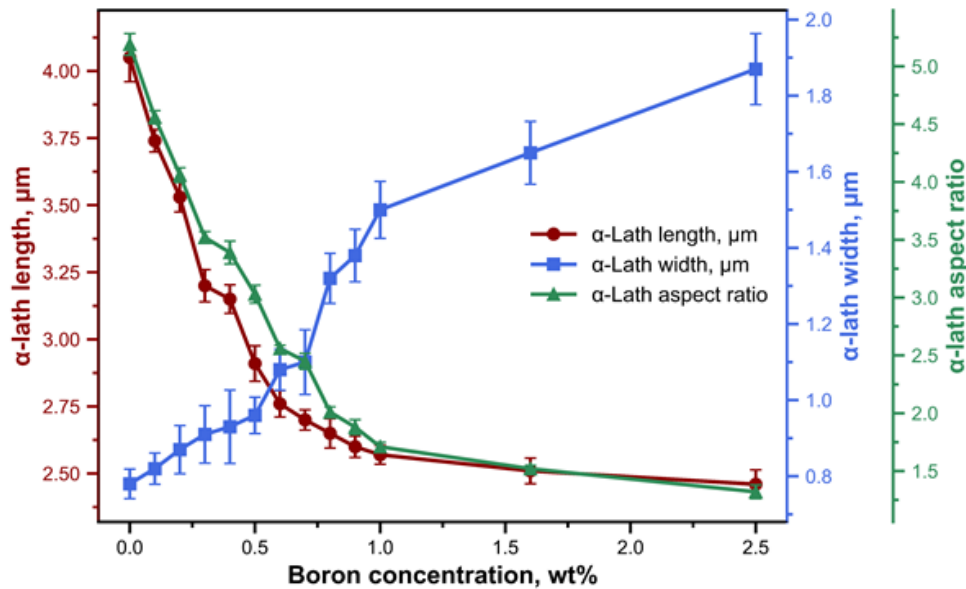


Figure 4-23 The impact of varying boron concentrations on the observed α -lath dimensions in surface laser glazed Ti6Al4V-xB alloy compositions.

4.4 Laser Glazed Ti6Al4V-0.1B: Effect of Process Parameters

4.4.1 Hardness and Melt Pool Variations

To comprehend how laser exposure time, aka laser scan speed, affects the hardness of laser glazed Ti6Al4V and Ti6Al4V-0.1B alloys, nanoindentation tests were performed on laser remelted regions of all samples, as illustrated in Figure 4-24. Nanohardness measurements were conducted on five different melt pools, with each pool subjected to 10 indents. Figure 4-24(a) displays the nanoindentation load – penetration depth curves for the polished cross-sections of Ti6Al4V and Ti6Al4V-0.1B parts. The data clearly show that, for the base alloy, the indentation depth increases as the exposure time is increased from 30 μs to 120 μs . Conversely, for the boron-modified alloy, the indentation depth decreases with the same increase in exposure time. The increase in indentation depth for the base alloy suggests a reduction in its average nanohardness value, potentially due to coarsening of the martensite laths. Figure 4-24(b) illustrates the variation in nanohardness and reduced modulus for Ti6Al4V and Ti6Al4V-0.1B parts across different exposure times used. For the base alloy, both nanohardness and reduced modulus exhibited a decreasing trend with increasing exposure time. The nanohardness decreased from approximately 4.1GPa at an exposure time of 30 μs to around 3.7GPa at an exposure time of 120 μs . Similarly, the reduced modulus dropped from about 119GPa to roughly

102GPa over the same range of exposure times. In contrast, the Ti6Al4V-0.1B alloy showed an increasing trend in both properties with longer exposure times. The nanohardness rose from about 4.5GPa at an exposure time of 30 μ s to approximately 5.7GPa at an exposure time of 120 μ s. The reduced modulus also increased significantly, from around 121GPa to about 145GPa. Clearly, the hardness increased progressively with the addition of boron for sample processed with the same exposure time. The enhanced surface hardness is attributed to the hardening effect of TiB precipitates in the microstructure. However, the estimated hardness based on the rule of mixtures was not as high as the measured value, indicating a significant contribution from grain refinement. The variation in exposure time, combined with boron addition, likely caused a refinement of the laser-glazed microstructure, further enhancing the hardness of the alloy beyond predictions from the rule of mixtures alone. The measured increase in hardness for boron-added samples with increased exposure time suggests that the rise was primarily due to grain refinement induced by the addition of boron, rather than solely the presence of TiB particles.

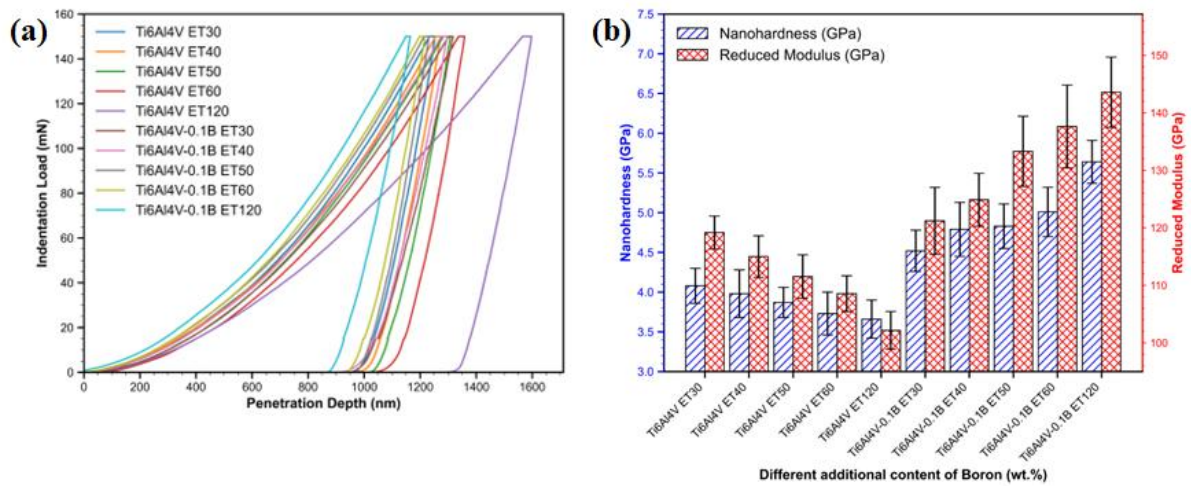


Figure 4-24 (a) load-penetration depth curves; (b) calculated nanohardness (H_d) and Reduced modulus (E_r) values of samples fabricated with different laser exposure time.

Figure 4-25 illustrates the impact of laser exposure time on the melt pool depth for Ti6Al4V and Ti6Al4V-0.1B alloys. It is evident that the melt pool depth increased with longer laser exposure times for both alloy compositions. The addition of 0.1 wt.%B to Ti6Al4V resulted in consistently deeper melt pools compared to the unmodified Ti6Al4V alloy, across all exposure times tested. The data showed that increasing the laser exposure time from 30 μ s to 120 μ s significantly enhanced the melt pool depth, suggesting a transition from conduction mode to keyhole mode melting. This transition was also marked by the formation of characteristic keyhole pores in the cross-sections of samples exposed to the longest exposure time of 120 μ s. The linear relationship between melt pool depth and laser exposure time was clear for both Ti6Al4V and Ti6Al4V-0.1B alloys, indicating that laser exposure time was a critical factor in controlling melt pool characteristics. The addition of boron appeared to augment the

effectiveness of laser in deepening the melt pool, highlighting its potential role in optimizing the laser processing of titanium alloys for improved microstructural properties.

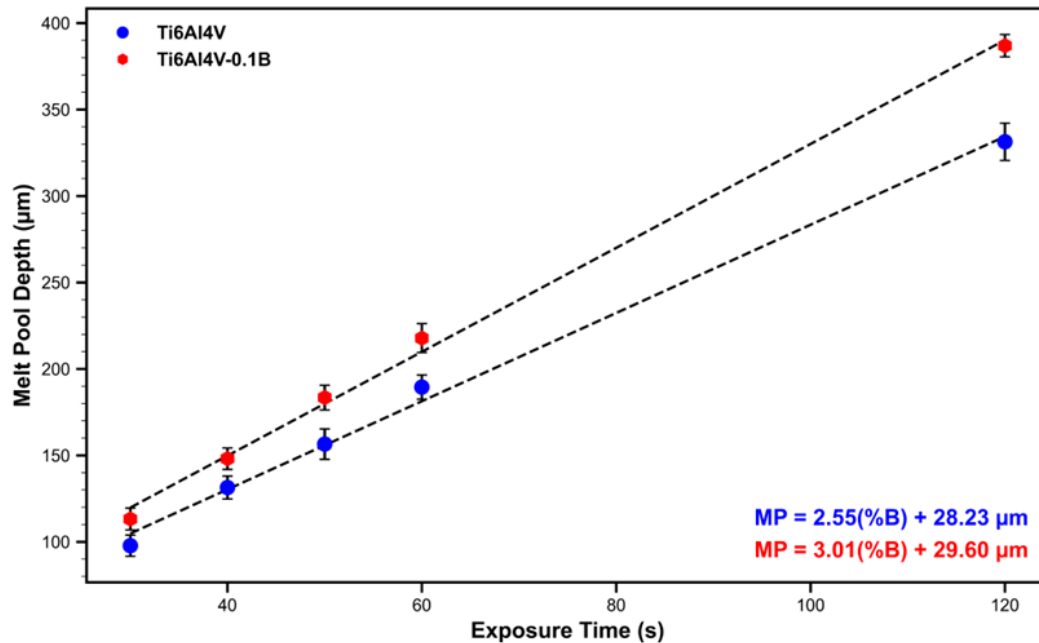


Figure 4-25 Variation of melt pool depth as a function of exposure time used in surface laser glazing.

4.4.2 Phase Identification and Analysis

The XRD spectrum in Figure 4-26 reveals the phase constituents of surface laser-glazed Ti6Al4V and Ti6Al4V-0.1B alloys subjected to various laser exposure times. The diffraction patterns reveal that both alloys predominantly consist of martensitic α' -titanium phase. No significant peaks corresponding to TiB, or β -Ti phases are observed, indicating that the laser glazing process primarily resulted in the formation of martensitic α' -titanium phase regardless of the laser exposure time or the addition of 0.1 wt.%B. It is possible that TiB phases could present but remained undetected due to the detection limits of XRD. Despite the samples exhibiting only α' -titanium phase, the XRD peaks showed shifts in 2θ values depending on the exposure time, as well as peak broadening. These shifts and broadening indicate variations in the lattice parameters and crystallite size, respectively, suggesting that laser exposure time influences the internal stress and microstructural refinement within the martensitic α' phase. The increase in peak intensity in samples, especially Ti6Al4V ET50, could be attributed to a highly preferred orientation (texture) in these samples, resulting from the laser processing. This preferred orientation implies that certain crystallographic planes are more aligned relative to the sample surface, enhancing the diffracted intensity for these planes. Additionally, a peak observed around 29° corresponds to plasticine used to hold the samples in the sample holder. This is an extrinsic error and should not be confused with the TiB phase. The presence of the plasticine peak indicates an artefact from the sample preparation process, which does not affect the intrinsic phase analysis of the alloys.

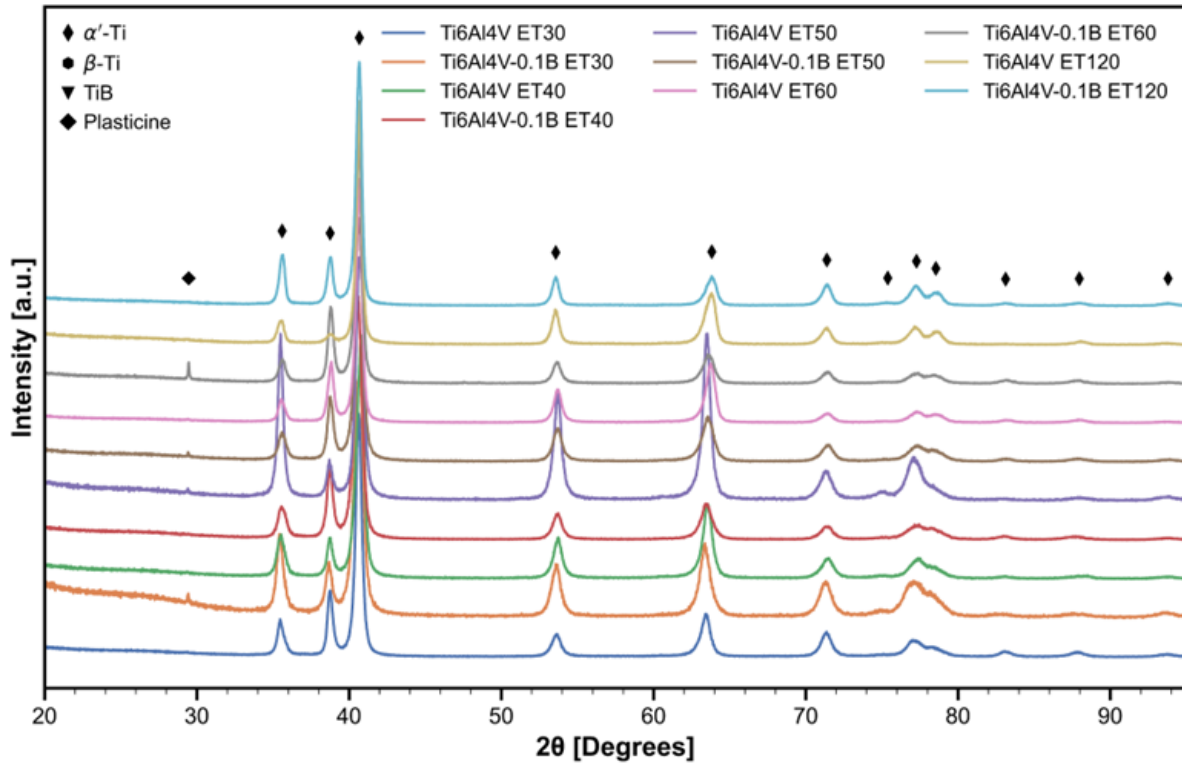


Figure 4-26 XRD spectrum displaying the phases present in surface laser-glazed Ti6Al4V and Ti6Al4V-0.1B alloys exposed to different laser exposure time.

The Rietveld analysis data for Ti6Al4V and Ti6Al4V-0.1B alloys at various exposure times shown in Table 4-1 indicates significant microstructural changes. For the base alloy, the 2θ peak position for the strongest α' -titanium initially increased from 40.52° at $30\mu\text{s}$ to 40.74° at $50\mu\text{s}$, then decreased slightly to 40.65° at $60\mu\text{s}$, and further to 40.49° at $120\mu\text{s}$. The d-spacing values followed the same trend as peak positions. The crystallite size increased significantly from 29.7 nm at $30\mu\text{s}$ to 65.1 nm at $120\mu\text{s}$, indicating substantial growth of crystallites. Concurrently, the microstrain decreased from 8.17×10^{-3} at $30\mu\text{s}$ to 5.73×10^{-3} at $120\mu\text{s}$, suggesting effective stress relief over longer exposure times. In the Ti6Al4V-0.1B alloy, the 2θ peak positions showed slight variations with different laser exposure times. As exposure time increases, there was a subtle shift to higher 2θ values up to $60\mu\text{s}$, followed by a slight decrease at $120\mu\text{s}$. Corresponding d-spacing values indicate subtle changes in the lattice parameter, which could be due to changes in the internal stress state of the samples. There was a clear trend of increasing crystallite size with increasing exposure time. This suggested longer exposure times promoted growth or coarsening of the crystallites in the martensitic microstructure. The microstrain in 0.1 wt.%B modified alloy decreased from 8.66×10^{-3} to 5.87×10^{-3} with increasing exposure time, though it generally remained higher than in the base alloy. Higher microstrain values typically indicate boron addition induces more lattice distortions.

Table 4-1 Quantitative Rietveld analysis of surface laser-glazed Ti6Al4V and Ti6Al4V-0.1B Alloys.

<i>Samples</i>	<i>2θ Values (°)</i>	<i>d (nm)</i>	<i>Crystallite Size (nm)</i>	<i>Microstrain (1×10^{-3})</i>
Ti6Al4V – ET30	40.512	0.2225	29.7	8.17
Ti6Al4V – ET40	40.721	0.2214	34.2	6.77
Ti6Al4V – ET50	40.742	0.2213	48.9	6.38
Ti6Al4V – ET60	40.654	0.2217	63.0	5.12
Ti6Al4V – ET120	40.493	0.2226	65.1	5.73
Ti6Al4V-0.1B – ET30	40.485	0.2226	33.1	8.66
Ti6Al4V-0.1B – ET40	40.514	0.2225	53.7	8.50
Ti6Al4V-0.1B – ET50	40.661	0.2217	55.9	8.46
Ti6Al4V-0.1B – ET60	40.530	0.2224	57.1	8.05
Ti6Al4V-0.1B – ET120	40.480	0.2227	60.5	5.87

4.4.3 Microstructural Analysis

Figure 4-27 presents SEM-BSE images of surface laser-glazed Ti6Al4V and Ti6Al4V-0.1B alloys subjected to different laser exposure times ranging from 30 μ s to 120 μ s. A typical hierarchical structure of acicular α' martensite was observed in the base alloy (Figure 4-27(a) – (e)) independent of the laser exposure time used. The primary α' martensite was extending across the entire prior- β grains, whose major and minor axes were tens and several micrometres, respectively. Numerous secondary α' martensite with major axis in a dozen micrometres and minor axis in hundreds of nanometres parallel or perpendicular to the primary α' martensite was also present in the microstructure. Finer tertiary α' martensite with major axis in several micrometres and minor axis in tens of nanometres or smaller were observed between secondary α' martensite in samples processed with higher laser exposure times. Moreover, at shorter exposure times for the case of 30 μ s and 40 μ s, the laths were relatively finer and more closely packed. As the exposure time increased further, the laths became more pronounced, wider and longer, indicating grain growth and coarsening of the martensitic structure. For Ti6Al4V-0.1B alloy (Figure 4-27(f) – (j)), the microstructure showed a more refined and complex morphology compared to the base alloy. Primary α' martensite was thinner and shorter than the that of the base alloy for the same processing conditions. In addition to the α' martensite, the microstructure displayed very fine structures in black contrast, confirmed as nanosized TiB precipitates. These features were more prominent at higher exposure times, especially in the samples produced with 60 μ s and 120 μ s exposure times.

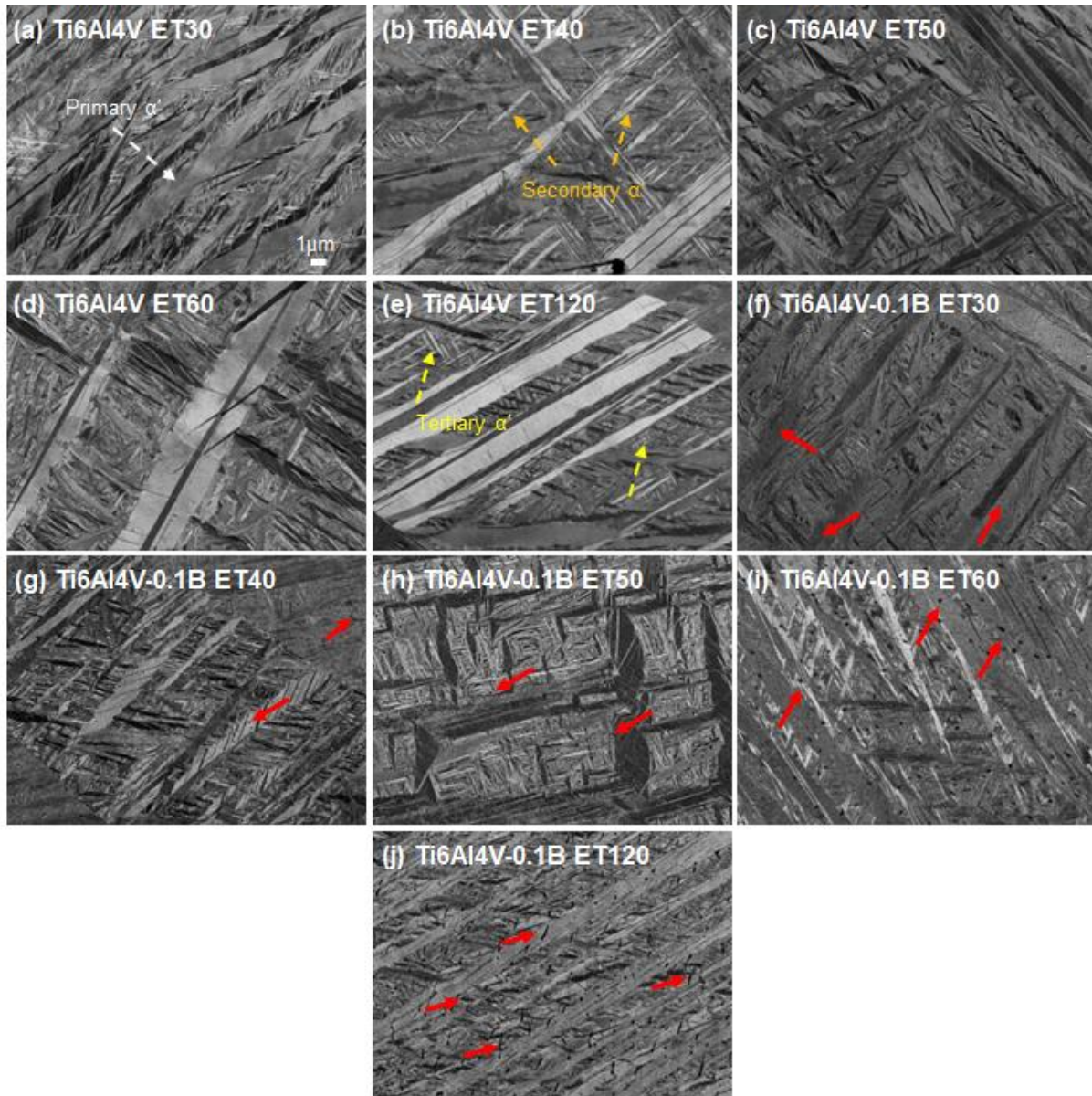


Figure 4-27 SEM-BSE images of surface laser-glazed (a) – (e) Ti6Al4V and (f) – (j) Ti6Al4V-0.1B alloy exposed to different laser exposure times. The red arrows indicate TiB precipitates present in the microstructure.

4.4.4 Reconstructed Prior- β Microstructure

Figure 4-28 shows the reconstructed prior- β grains of surface laser-glazed Ti6Al4V and Ti6Al4V-0.1B alloys subjected to different laser exposure times. Examination of these regions revealed distinct differences in grain behaviour between the two alloy compositions. For the base Ti6Al4V alloy (Figure 4-28(a) – (e)), there was no significant grain refinement observed in the laser remelted zones. While a few new grains were formed, the overall grain structure remained relatively coarse. It can be inferred that increasing the laser exposure time from 30 μ s to 120 μ s had a negligible effect on the prior β -grain size in the laser-glazed regions.

Consequently, epitaxial growth of columnar grains continued to dominate the microstructure, indicating limited impact of exposure time on grain refinement for this alloy. Through a series of experiments, an optimal boron content for achieving significant grain refinement in laser surface-glazed regions has been identified in this study. The findings indicated while higher levels of boron addition effectively refine prior β -grain sizes, a similar grain refinement effect could be achieved with lower boron content by precisely adjusting the laser exposure time. Figure 4-28 (f) – (j) illustrate the reconstructed prior β -grain structures in the laser remelted regions of the Ti6Al4V-0.1B alloy. At shorter exposure times up to 50 μ s, the remelted regions showed relatively coarse grains. As the exposure time increases to 50 μ s and beyond, the grain structure within the remelted zones showed some refined grains. Significant grain refinement was observed at longer laser exposure time of 120 μ s. At this exposure, the remelted regions exhibited finer and more uniform grains, indicating boron addition effectively promotes grain refinement during the laser glazing process.

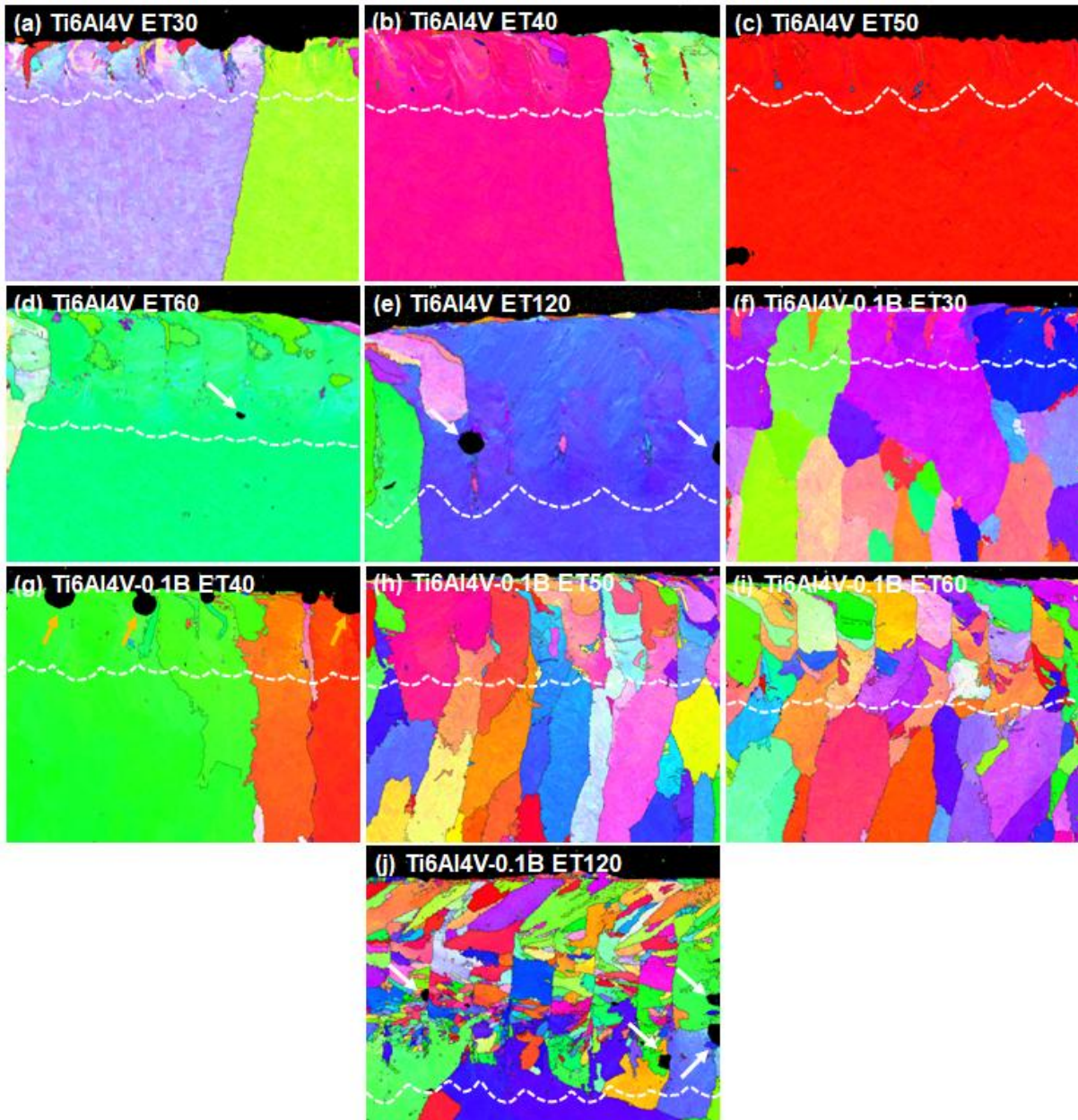


Figure 4-28 Reconstructed prior β -grain sizes of surface laser-glazed (a) – (e) base Ti6Al4V alloy; (f) – (j) Ti6Al4V-0.1B alloys exposed to different laser exposure times. The white dashed lines denote the melt pools formed during the laser glazing process. White arrows indicate the presence of keyholes, while orange arrows highlight surface imperfections resulting from sample cleaning.

4.5 Discussion

4.5.1 Accuracy of Nanoindentation

The accuracy of nanoindentation measurements in Ti6Al4V and 0.1 wt.%B-modified Ti6Al4V alloys is significantly influenced by multiple interconnected factors requiring meticulous calibration, careful experimental protocols, and advanced analytical techniques. Instrumental accuracy depends critically on maintaining tip geometry integrity to avoid artificial variations

in hardness and modulus measurements (Fischer-Cripps, 2004). Additionally, ensuring thermal drift stabilization (<0.05 nm/s) and mitigating surface roughness (asperities $<10\%$ indentation depth) are foundational practices to achieve reliable measurements (Menčík, 2012; Schuh, 2006).

Material-specific complexities further complicate accuracy. The pronounced anisotropy of α -titanium, a consequence of its hexagonal close-packed crystal structure, generates plane-dependent variations in mechanical properties, with the basal (0001) plane exhibiting significantly higher hardness than prismatic (10 $\bar{1}$ 0) planes due to restricted dislocation activities and specific slip system activations (Zhang et al., 2016; Wheeler et al., 2013). Such crystallographic orientation effects necessitate orientation-resolved nanoindentation via EBSD mapping (Pathak & Kalidindi, 2015) and crystal plasticity finite element modelling (CPFEM) for correcting isotropic assumptions commonly used in the Oliver-Pharr method (Kalidindi & Vachhani, 2014). In boron-modified Ti6Al4V alloys, additional accuracy concerns emerge from microstructural heterogeneity induced by TiB whisker formation. The stark hardness contrast between the TiB phase (~ 20 – 30 GPa) and the α -titanium matrix (~ 3 – 4 GPa) amplifies measurement scatter unless carefully correlated with phase identification through EBSD or EDS mapping (Sen et al., 2010; Zhang et al., 2018). Residual stresses, arising from differing coefficients of thermal expansion between TiB and the titanium matrix, further alter local mechanical responses, necessitating pre-test stress relief annealing or spatially resolved X-ray diffraction analysis to ensure accuracy (Oliver & Pharr, 1992).

Moreover, boron segregation at grain boundaries enhances local hardness through dislocation pinning, requiring spatially resolved statistical indentation approaches to separate intrinsic and extrinsic microstructural effects (Bhattacharya & Nix, 1988). The inherent anisotropic elastic behaviour of orthorhombic TiB whiskers (B27 structure) additionally impacts modulus accuracy depending on the indentation orientation relative to whisker axes (Y. Feng et al., 2017). Pile-up and sink-in artefacts caused by differing plastic deformation responses of ductile matrix regions versus brittle TiB whiskers necessitate atomic force microscopy to accurately recalibrate the contact area for the Oliver-Pharr analysis (Bolshakov & Pharr, 1998). Furthermore, the exceptional hardness of TiB whiskers accelerates diamond tip wear, artificially reducing measured hardness values over repetitive testing, necessitating periodic AFM-based tip geometry inspections or adopting harder tips such as cubic boron nitride (Fischer-Cripps, 2004).

Finally, achieving uniform surface finish in dual-phase composites poses significant preparation challenges, as differential polishing rates between TiB and matrix phases create topographical inconsistencies, thereby introducing additional measurement scatter. Electrolytic polishing or focused ion beam milling are recommended surface preparation methods to ensure minimal surface-induced errors (Menčík, 2012). Collectively, the accuracy of nanoindentation in boron-modified Ti6Al4V alloys demands a synergistic integration of precise instrumental

control, detailed crystallographic and phase mapping, advanced modelling corrections, and rigorous surface preparation protocols.

4.5.2 Influence of Boron on Solidification Process

Figure 4-29 shows the effect of boron addition on the solidification behaviour of Ti6Al4V-xB alloys. The solidification process curves near the melting temperature for representative Ti6Al4V-xB alloys were shown in Figure 4-29(a), which were calculated using JMatPro based on Scheil-Gulliver solidification model. The addition of boron considerably reduces the precipitation temperature of β phase and largely expands the freezing range of the alloy when aluminium and vanadium concentration was fixed at 6 wt.% and 4 wt.%, respectively. Ti6Al4V had a very narrow freezing range of about $\sim 13\text{K}$, as reported in elsewhere (Lin et al., 2007). The narrower freezing range aligns the solidification behaviour of the alloy with that of a pure metal, resulting in the rapid solidification of prior- β grains during cooling. Consequently, the prior- β grains exhibit epitaxial growth, expanding throughout the solidified sample. However, a narrow freezing range helps reduce the likelihood of solidification cracking and micro-separation (X. Tan et al., 2015). The freezing range of Ti6Al4V-xB alloys increases with increasing boron concentration as shown in Figure 4-29(c). The addition of 0.1 wt.% B significantly extends the freezing range of the base alloy, increasing it by approximately 18 times. This prolongs the solidification period and creates greater constitutional supercooling at the front of the solidifying interface. The relationship between freezing range and the constitutional supercooling can be given as follows (A. Xue et al., 2019):

$$\frac{G}{R} < \frac{m_l C_0 (1 - k_0)}{D_L k_0} = \frac{\Delta T}{D_L} \quad 4.11$$

In this context, G represents the temperature gradient, R denotes the solidification rate, m_l is the liquidus slope, C_0 refers to the solute concentration in weight percent, k_0 signifies the solute partition coefficient, D_L indicates the diffusivity of the solute in the liquid, and ΔT represents the freezing range. A wide freezing range caused by the addition of boron promotes the initiation of constitutional undercooling, as supported by Equation 4.11, and facilitates the columnar to equiaxed transition (Lin et al., 2007). Moreover, boron is α -stabiliser and β -transus temperature is increased by the addition of boron to expand $\alpha+\beta$ phase region. Figure 4-29(b) illustrates the relationship between temperature and β -phase fraction for the base Ti6Al4V alloy and its variants with different boron contents. The addition of boron has a noticeable impact on the β -phase fraction. With increasing boron content, the curves showed subtle deviations from the base alloy, suggesting boron influences the solidification process and phase transformation. The observed decrease in the fraction of the β -phase with increasing boron content can be attributed to several factors. Firstly, boron acts as an α -phase stabilizer in titanium alloys, which means it expands the temperature range over which the α -phase is stable, thereby reducing the stability range of the β -phase. Additionally, boron readily forms TiB during solidification. These TiB compounds consume a significant amount of liquid titanium that would otherwise

contribute to the formation of the β -phase, resulting in a lower fraction of the phase. Furthermore, the solidification pathway changes with boron content. For hypereutectic compositions, TiB forms directly from the liquid phase before the β -phase, reducing the available titanium for β -phase to be formed. Consequently, these factors collectively lead to a decreased fraction of the β -phase as the boron content increases. The addition of boron to Ti6Al4V alloy results in a modest increase in the β_{transus} temperature, rising from 942°C to 956°C with 2.5 wt.%B, as seen in Figure 4-29(d). This slight elevation can be attributed to the limited solubility of boron in the titanium matrix, where boron primarily forms TiB rather than significantly altering the matrix composition. The formation of TiB consumes titanium atoms, which impacts the phase equilibrium to some extent but does not cause a dramatic increase in the β transus temperature (Ma et al., 2021). Additionally, role of boron as an alpha stabilizer is relatively weak compared to other elements, leading to only a minor shift in the transus temperature. Therefore, the modest increase in the β transus temperature reflects the limited influence of boron on the overall phase stability of the alloy.

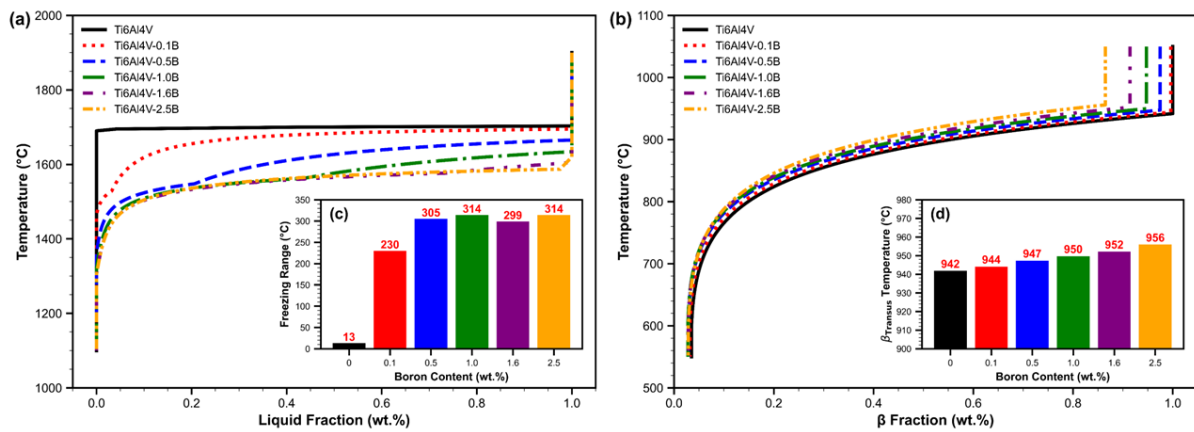


Figure 4-29 Effect of boron concentration on solidification behaviour of Ti6Al4V-xB alloys: solidification curves (a) near the melting temperature; (b) near the β_{transus} temperature. The insets illustrate (c) the freezing range and (d) the transus temperature.

The solidification during the arc melting process occurred under non-equilibrium cooling conditions. The phase transformation processes of Ti6Al4V after the addition of 1.0 wt.%B was simulated by JMatPro and the phase fraction results are shown in Figure 4-30. As revealed in Figure 4-30(a), the β -titanium phase solidifies first from the molten liquid at 1634°C. Simulation results further indicated for the other alloy compositions that for hypoeutectic alloys, the β phase is the first to precipitate, whereas for hypereutectic alloys, TiB is the first phase to form during non-equilibrium solidification. The $\beta \rightarrow \alpha$ phase transformation starts at about 950°C and finishes at 600°C. The formation of TiB precipitates is shown in Figure 4-30(b). As the temperature decreased to 1562°C, TiB began to precipitate out from the remained liquid, and the mass fraction of TiB phase reaches the maximum value of 5.31% at 600°C.

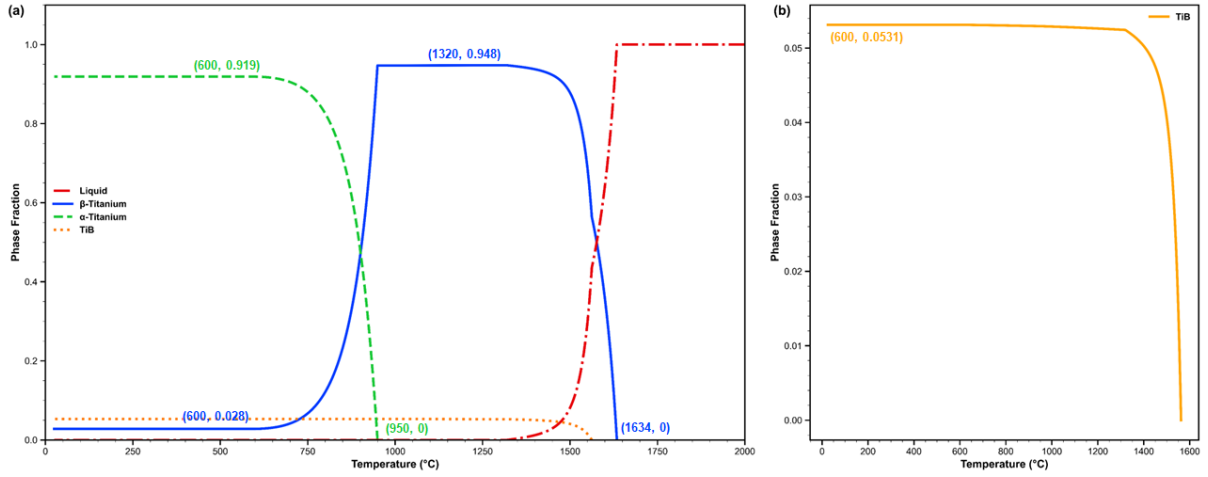


Figure 4-30 (a) non-equilibrium solidification behaviour of Ti6Al4V-1.0B alloy; (b) TiB precipitate

4.5.3 Microstructure Formation

According to the Ti6Al4V-B phase diagram (Figure 4-31(a)), the solidification process within the hypoeutectic region follows the path: $L \rightarrow L + \text{primary } \beta\text{-Ti} \rightarrow \text{primary } \beta\text{-Ti} + \text{eutectic } (\beta\text{-Ti} + \text{TiB}) \rightarrow \alpha\text{-Ti} + \beta\text{-Ti} + \text{TiB}$. Initially, primary β -titanium precipitates from the Ti6Al4V liquid (Figure 4-31(b1)), causing boron to be expelled at the solid/liquid interface, leading to its segregation around the β -titanium nuclei (Pan et al., 2022). As solidification advances, primary β grains grow, and eutectic TiB precipitates at the boundaries of these primary β grains as the temperature decreases to the eutectic point (Figure 4-31(c1)). The presence of TiB reinforcements at the primary β grain boundaries inhibits the growth of these grains, resulting in refined β grains compared to those in the Ti6Al4V alloy. In regions where TiB whiskers do not precipitate, coalescence of adjacent primary β grains occurs (Figure 4-31(d1)). Consequently, the alloy exhibits a discontinuous network microstructure, as depicted in Fig. 12d1. Upon further cooling below the $\beta \rightarrow \alpha$ transformation temperature, the $\beta \rightarrow \alpha$ phase transformation takes place, preserving the discontinuous network structure, as shown in Figure 4-31(e1).

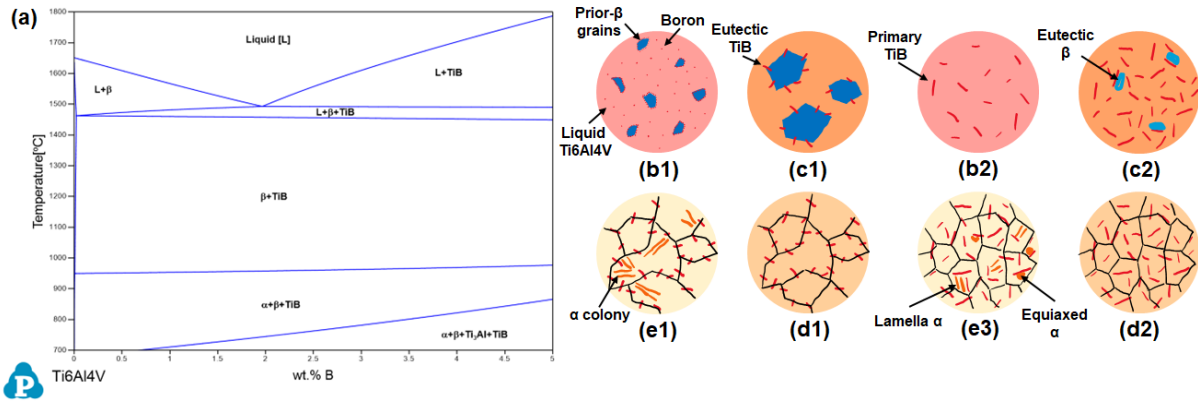


Figure 4-31 A schematic representation of the Ti6Al4V–B phase diagram, illustrating the mechanism of microstructure formation (b1-e1) in hypoeutectic alloy; and (b2-e2) hypereutectic alloy.

The solidification pathway in the hypereutectic region, as depicted by the Ti6Al4V–B phase diagram (Fig. 12a), follows the sequence: $L \rightarrow L + \text{primary TiB} \rightarrow \text{primary TiB} + \text{eutectic } (\beta\text{-Ti} + \text{TiB}) \rightarrow \alpha\text{-Ti} + \beta\text{-Ti} + \text{TiB}$. Upon cooling to the $L + \text{TiB}$ region, primary TiB precipitates from the liquid phase (Figure 4-31(b2)). As the temperature further decreases to the eutectic point, the eutectic mixture of $\beta\text{-Ti}$ and TiB forms. Due to the non-equilibrium nature of rapid cooling solidification processes (Armstrong et al., 2022; Hayat et al., 2019), primary TiB acts as nucleation sites for eutectic $\beta\text{-Ti}$ during the eutectic reaction (Figure 4-31(c2)), resulting in the presence of TiB at the β grain boundaries (Figure 4-31(d2)). Some primary TiB whiskers become embedded within the β grains because of the slow mobility of TiB (Z. Zhou et al., 2021) (Figure 4-31(e2)). Although some eutectic TiB precipitates at the β grain boundaries during the eutectic process, the majority of TiB whiskers are primary due to solidification occurring in the hypereutectic zone. Upon further cooling, the transformation from β to α phase takes place.

As reported in several studies, in-situ formed TiB in Ti6Al4V can have orientation relationships with the α and β phases (R. Banerjee et al., 2004, 2005; Feng, Zhou, Jia, Meng, et al., 2006; Genç et al., 2006; Ozerov et al., 2017; Y. F. Yang et al., 2013). In this work the EBSD scan was successfully used to detect and confidently identify the presence of TiB phase. While most of the identified TiB phases had no specific orientation relationships with their surrounding α phases, some were observed to follow one of the orientation relationships reported in the literature (R. Banerjee et al., 2004b, 2005; Feng, Zhou, Jia, Meng, et al., 2006b; Genç et al., 2006; Hill et al., 2005b; Y. F. Yang et al., 2013). This study examines three types of orientation relationships (ORs) between the TiB and α phases (Le et al., 2022; D. X. Li et al., 1993; Sasaki et al., 2011):

- OR-I: $(0001)_{\alpha} \parallel (001)_{\text{TiB}}$ and $[1\bar{2}10]_{\alpha} \parallel [010]_{\text{TiB}}$
- OR-II: $(0001)_{\alpha} \parallel (201)_{\text{TiB}}$ and $[1\bar{2}10]_{\alpha} \parallel [010]_{\text{TiB}}$
- OR-III: $(10\bar{1}0)_{\alpha} \parallel (201)_{\text{TiB}}$ and $[1\bar{2}13]_{\alpha} \parallel [010]_{\text{TiB}}$

Figure 4-32(a) displays the superposition of the inverse pole figure (IPF) of the β phase with the band contrast map of the α phase and TiB in a Ti6Al4V-1.0B arc-melted alloy. Figure 4-32(b) shows the band contrast map overlaid with the TiB phase map, highlighting the phase boundaries between TiB and the α phase with different preferred misorientations (OR-I, OR-II, and OR-III) using distinct colour lines. Multiple ORs between TiB and the α phase are evident. Figure 4-32(c)-(e)-(g) and Figure 4-32(d)-(f)-(h) present the pole figures of the TiB and α phases with OR-I (Figure 4-32(c) and (d)), OR-II (Figure 4-32(e) and (f)), and OR-III (Figure 4-32(g) and (h))), respectively, also showing the pole figures of the adjacent β phases. A Burgers OR is observed between the three α precipitates (α -Ti₁, α -Ti₃, and α -Ti₅) and the neighbouring β phases (Figure 4-32(c)-(e)-(g)). However, the other three α precipitates (α -Ti₂, α -Ti₄, and α -Ti₆) do not exhibit any OR with the neighbouring β phases (Figure 4-32(d)-(f)-(h)). The preferred OR between the TiB and β phase is likely because the hypereutectic TiB acts as nucleation sites for the β phase. When an OR exists between TiB and the β phase, the α precipitates tend to maintain OR with both TiB and the β phase, resulting in a lamellar microstructure. Conversely, when the α precipitates exhibit OR with TiB but not the Burgers OR with the β phase, they are more likely to develop an equiaxed morphology (Le et al., 2022; Nandwana et al., 2012). Consequently, both α lamellae and equiaxed α grains form due to the presence or absence of OR between TiB and the β phase.

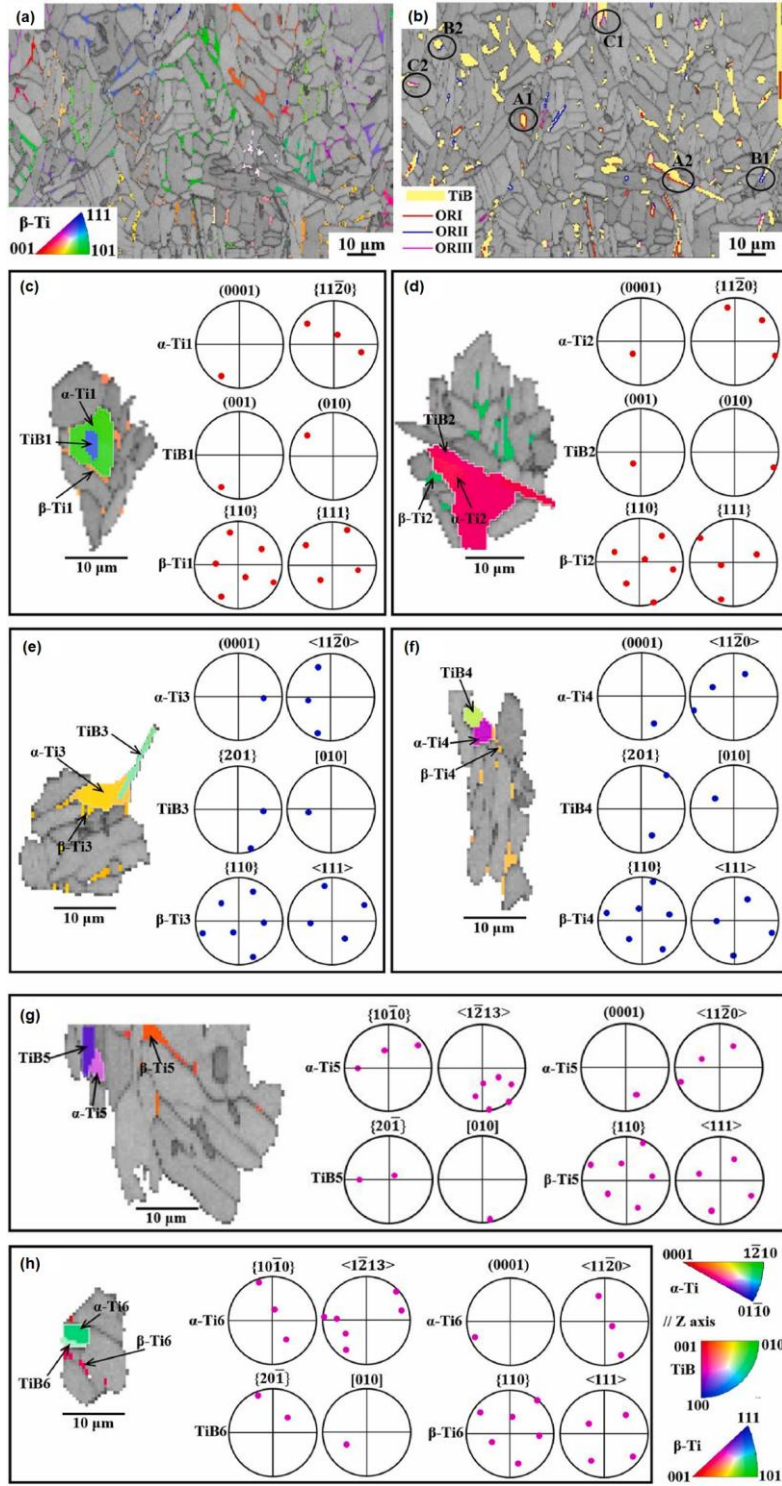


Figure 4-32 (a) Superimposed IPF map parallel to Z axis of the β phase and band contrast maps of the α phase and TiB within Ti6Al4V-1.0B alloy after arc melting; (b) superimposed phase distribution map of TiB and band contrast maps of the α and β phases, highlighting the phase boundaries between TiB and the α phase with different preferred misorientations (OR-I, OR-II, and OR-III) delineated by distinct colour lines. (c) - (f) - (g) and (d) - (f) - (h) present IPFs ($\parallel$ Z axis) and pole figures for the TiB, α , and β phases in the circular regions marked A1-C1 and A2-C2 in (b).

The addition of boron to titanium alloys has a significant impact on the formation and distribution of grain boundary α precipitates. Boron, even in small quantities, can alter the microstructural evolution of these alloys by affecting the nucleation and growth processes of α phase at the grain boundaries. This modification is primarily due to the solute pinning effect of boron atoms, which segregate at grain boundaries and interfaces, thereby influencing the overall grain boundary dynamics. To explain the observed changes in grain boundary α precipitates with varying boron content, a 'boron solute pinning mechanism' is proposed, as schematically illustrated in Figure 4-33. In the base Ti6Al4V alloy (Figure 4-33(a)), when the temperature drops below T_β , grain boundary α precipitates start to nucleate at the prior β grain boundary (step (2)) and then rapidly grow along the grain boundary until they impinge on each other (step (3)). The energy barrier for the growth of grain boundary α precipitates is generally much lower than that for nucleation, resulting in a limited number of grain boundary α precipitates along a single straight grain boundary in the base alloy. In contrast, the Ti6Al4V-0.1B alloy (Figure 4-33(b)) exhibits a different behaviour due to the addition of 0.1 wt.%B. At temperatures above T_β (step (4)), most boron solutes are distributed at the prior β grain boundaries (as indicated by Auger electron spectroscopy results in reference(Luan et al., 2015b)), which helps retard the growth of β grains at high temperatures. As the temperature decreases below T_β , grain boundary α precipitates begin to nucleate at the prior β grain boundary (step (5)). Due to the negligible solubility of boron solutes in the α phase, excess boron solutes are rejected from the newly formed grain boundary α precipitates and segregate at the interface between grain boundary α and β grains on both sides (step (5)). The segregated boron solutes at the α/β interface significantly restrict the growth of grain boundary α precipitates compared to the base alloy. Under these conditions, the energy barrier for the growth of grain boundary α precipitates can become comparable to that required for nucleation (step (6)). Consequently, the enhanced nucleation and restricted growth of grain boundary α result in an increased number of grain boundary α precipitates in the Ti6Al4V-0.1B alloy. As the boron content increases further, the grain boundary α fraction decreases and may even disappear, as depicted in Figure 4-33. This suggests that while a small addition of boron enhances the nucleation of grain boundary α precipitates, higher concentrations lead to a reduction or elimination of these precipitates due to the increased segregation and pinning effects of boron solutes.

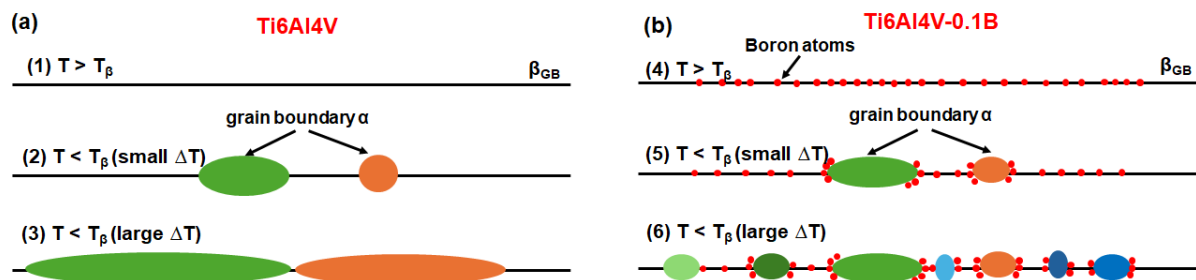


Figure 4-33 Schematic diagrams depict the influence of boron segregation at the α/β phase boundary on the precipitation behaviour of grain boundary α in two alloys: (a) Ti6Al4V and (b) Ti6Al4V-0.1B. In these illustrations, stages (2) and (5) indicate the nucleation of grain boundary α precipitates occurring with a smaller degree of supercooling, while stages (3) and (6) represent the growth process of these precipitates under conditions of greater supercooling.

4.5.4 Effect of Boron Addition to Prior- β Microstructure

Additives predominantly influence the formation of equiaxed grains in titanium alloys through two primary mechanisms: enhancing constitutional supercooling and offering potential nucleation sites. It is well established that supercooling is crucial for equiaxed grain formation. Among the various forms of supercooling, including thermal and curvature supercooling, constitutional supercooling is the most significant, rendering the effects of other types negligible. According to the constitutional supercooling criterion (Equation 4.11), an increase in the freezing range intensifies constitutional supercooling under constant solidification conditions (solidification velocity R and temperature gradient G), facilitating the formation of equiaxed grains. Consequently, the influence of an additive on constitutional supercooling is mediated by its effect on the freezing range, ΔT . Similar to other effective additives reported in the literature, such as Ni (Sui et al., 2021; Xiong et al., 2021), Si (Merceddy et al., 2017), and Cu (D. Zhang et al., 2019), boron addition can significantly broaden the freezing range and more effectively enhance constitutional undercooling.

M. J. Bermingham et al., 2019 identified two essential criteria for a potential nucleation site. Firstly, the crystallographic orientation of the nucleation site must closely align with that of the growing solid phase. For example, the crystallographic alignment between La_2O_3 and β -titanium makes La_2O_3 an advantageous nucleation substrate for β -titanium during solidification (M. J. Bermingham et al., 2019). This alignment-based favourability was similarly observed in a study utilizing boron additives to promote equiaxed grain formation, where TiB effectively served as a nucleation substrate due to its orientational relationship with β -Ti (A. Xue et al., 2019). Secondly, the particle size of the potential nucleation sites is critical; larger particles are more effective. Smaller particles exhibit a high nucleant particle potency (ΔT_N), making it challenging for supercooling to surpass ΔT_N , thereby inhibiting stable grain formation. Bermingham et al. determined that particles smaller than $1\mu\text{m}$ are generally ineffective as nucleation sites due to the high ΔT_N , compounded by latent heat and recoalescence effects (M. J. Bermingham et al., 2019). In the present study, it was observed that nano-sized TiB particles

were present in the microstructure, and their volume increased with the increasing boron concentration. This indicates that, contrary to previous assumptions, nano-sized TiB particles can serve as effective nucleation substrates when their concentration is sufficiently high, and it forms before β -titanium. Therefore, both spontaneous nucleation and heterogeneous nucleation facilitated by TiB particles should be considered in this context. However, if TiB forms after β -Ti phase, only spontaneous nucleation is considered viable in this context.

An interdependence model for predicting grain size was formulated by StJohn et al. (Stjohn et al., 2011). This model has been effectively employed by Bermingham et al. (M. J. Bermingham et al., 2019) and Zhang et al. (S. Zhang et al., 2021) to analyse the evolution of grain morphology during the solidification of Ti3Al8V6Cr4Mo4Zr + La₂O₃ and Ti5Al2Sn2Zr4Mo4Cr, respectively. The interdependence model, represented by equation 4.12, considers three critical factors in determining grain size: the alloy composition, the potency of nucleating particles, and the spacing between particles.

$$d_{gs} = \frac{D_L \times \Delta T_N}{R \times Q} + \frac{4.6 \times D_L}{R} \left(\frac{C_1^* - C_0}{C_1^* (1 - k)} \right) + X_{SD} \quad 4.12$$

$$= X_{CS} + X_{DL} + X_{SD}$$

where D_L denotes the diffusion coefficient within the liquid metal, while ΔT_N signifies the critical nucleation supercooling for the most probable particles. The term R represents the growth velocity, and Q stands for the growth restriction factor. The symbol C_1^* refers to the composition of the liquid metal at the solid-liquid (S/L) interface, whereas C_0 is the overall composition of the alloy. The partition coefficient is denoted by k . The parameter X_{CS} indicates the distance that an initial grain must grow to induce sufficient constitutional supercooling ΔT_{CS} to nucleate a new grain. The term X_{DL} represents the distance from the S/L interface to the point where ΔT_{CS} is adequate to nucleate a new grain, and X_{SD} measures the distance from X_{DL} to the nearest potential nucleation particle. According to classical nucleation theory, grain growth occurs only if the grain size exceeds a critical threshold. It is assumed that the addition of boron has a negligible impact on the nucleation site density. Therefore, in equation 4.12, ΔT_N is defined as the nucleation supercooling corresponding to this critical grain size, which remains constant.

Figure 4-34 illustrates the grain morphology evolution in Ti6Al4V alloys with varying boron additions, based on the inter-dependence model. Two potential nucleation sites ahead of the S/L interface are identified for detailed analysis. In scenarios of low boron content, depicted in Figure 4-34(a), the temperature gradient, G_L , at the initial nucleation site is steep, leading to low constitutional supercooling that does not meet the critical nucleation supercooling threshold ($\Delta T_{CS1} < \Delta T_N$). Consequently, the first nucleation site fails to develop sufficiently to form a new grain. As solidification progresses, the temperature gradient at the S/L interface decreases. At the second potential nucleation site, the constitutional supercooling surpasses the critical

nucleation undercooling ($\Delta T_{CS1} \geq \Delta T_N$), allowing a new grain to form. The emergence of new grains disrupts the epitaxial growth of initial grains, with the initial grain size determined by $X'_{CS1}(\text{initial}) + X'_{DL1}$. This process repeats until solidification process finishes, determining the size of all grains by $X_{CS} + X_{DL}$. Initially, low constitutional supercooling and high G value result in a large $X'_{CS1}(\text{initial})$, leading to large initial grain sizes. Bermingham et al. reported that subsequent nucleation sites have much smaller X_{CS} , promoting the formation of smaller equiaxed grains (M. J. Bermingham et al., 2019). Therefore, the final microstructure of the Ti6Al4V-xB alloys is expected to comprise both large columnar grains and small equiaxed grains. As the boron content increases, the freezing range broadens, thereby enhancing the constitutional supercooling. At the initial nucleation site, the constitutional supercooling may still surpass the critical supercooling threshold despite a high temperature gradient (G), as illustrated in Figure 4-34(b). Specifically, ΔT_{CS2} remains greater than or equal to ΔT_N , allowing the primary nucleation site to continue growing progressively and forms a new grain. In this scenario, the sum of $X'_{CS2}(\text{initial})$ and X'_{DL2} is less than the sum of $X'_{CS1}(\text{initial})$ and X'_{DL1} . Consequently, the size and aspect ratios (length to width) of the initial grains decrease with increasing boron content.

Moreover, two additional factors must be considered. The first factor is the insufficiency of nucleation sites generated through spontaneous nucleation. As illustrated in Figure 4-34, if potential particle 1 is assumed to be absent and potential particle 2 is the closest nucleation site, then under conditions of high boron content, even when the constitutional supercooling (ΔT_{CS}) surpasses the critical nucleation undercooling (ΔT_N), the formation of new grains is hindered due to the scarcity of nucleation sites. Consequently, the initial grains will continue to grow until they encounter potential particle 2. This implies that titanium alloys with either low or high boron content may exhibit similar grain sizes owing to the insufficient nucleation sites. The second factor is the behaviour of the nucleation rate and growth rate (R), which initially increase and then decrease as supercooling intensifies (Kurz et al., 2023). Thus, high boron content may result in a reduction in both nucleation and growth rates, ultimately leading to an increase in the final grain size.

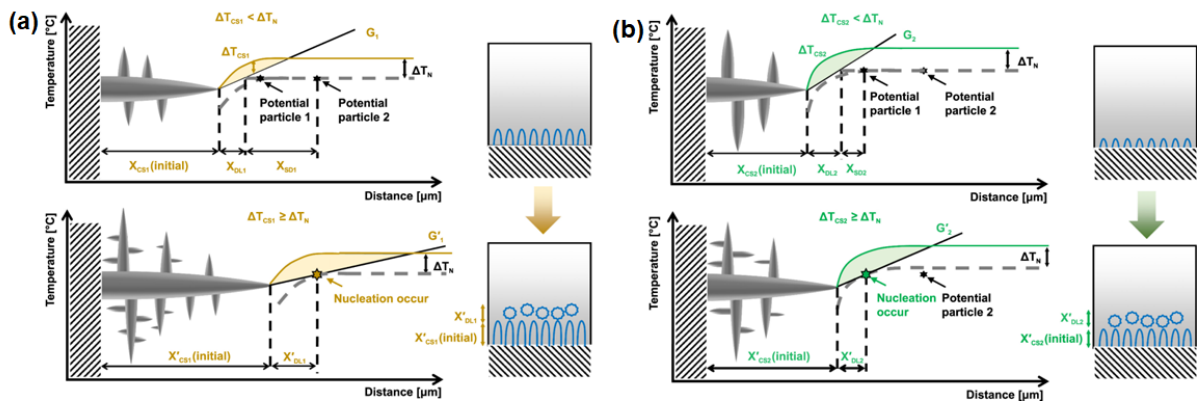


Figure 4-34 Schematic of effect of boron concentration on grain refinement; (a) low boron concentration; (b) high boron concentration.

4.5.5 Formation of TiB Network Structure

The distribution of the boron element during solidification is crucial for understanding the formation and distribution of TiB. JMatPro software was utilized to simulate and analyse the solute distribution of aluminium, vanadium, and boron at the S/L interface in Ti6Al4V and Ti6Al4V-0.3 wt.%B alloys during solidification. The findings, depicted in Figure 4-35(a) – (b), reveal that during the solidification of melt pool, the addition of boron and increased supercooling cause boron to accumulate on the liquid side of the S/L interface. This phenomenon also intensifies the segregation of aluminium and vanadium. The simulated data offer critical insights into the solute redistribution dynamics. In Figure 4-35(a), the concentrations of aluminium and vanadium remain relatively constant throughout the solidification process, indicating minimal segregation. However, Figure 4-35(b), which includes boron in the alloy, shows a significant change in solute behaviour. Segregation profile of boron highlights a marked accumulation in the liquid phase as solidification progresses. This behaviour can be attributed to several metallurgical principles. The partition coefficient (k) governs solute distribution between the solid and liquid phases. For many solutes, including boron, k is less than the unity, indicating a higher solubility in the liquid phase. Consequently, boron is preferentially rejected into the liquid during solidification. The addition of boron may also lead to increased supercooling. Higher supercooling rates enhance the driving force for nucleation and can significantly affect the growth dynamics of the solidifying phase. Rapid solidification processes, such as laser processing, result in high cooling rates, limiting the time available for solute diffusion. This rapid cooling intensifies solute segregation, especially for elements with low partition coefficients. In this case, boron is rapidly rejected into the liquid phase, accumulating at the S/L interface as solidification proceeds. The sharp increase in boron concentration near the end of solidification, as depicted in Figure 4-35(b), indicates that boron is being enriched in the remaining liquid. As solidification nears completion, the last regions to solidify, such as intercellular and interdendritic regions, exhibit higher boron concentrations. Additionally, the presence of boron influences the segregation behaviour of aluminium and vanadium. The curves for these elements in Figure 4-35(b) differ from their behaviour in Figure 4-35(a), suggesting that the increased supercooling and boron addition alter their distribution as well.

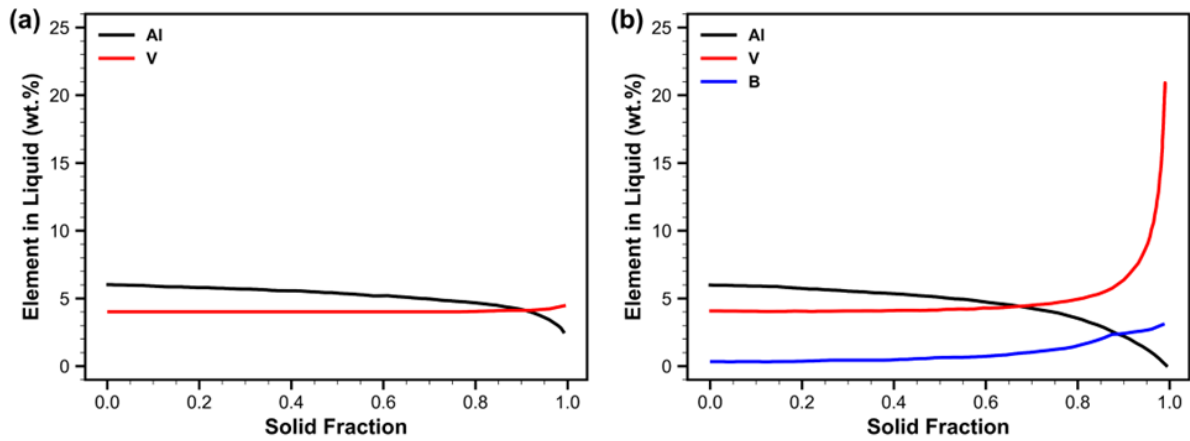


Figure 4-35 JMatPro simulation results for solute distribution during the solidification of (a) Ti6Al4V; and (b) Ti6Al4V-0.3 wt.%B alloy.

The variation in boron concentrations within the melt pool induces distinct fluid convection patterns, resulting in diverse microstructures. At relatively low boron concentrations, TiB is predominantly distributed along grain boundaries, as shown in Figure 4-18(c). This phenomenon can be attributed to the reduced turbulence in the melt pool under these conditions, which causes non-uniform boron enrichment, as illustrated in Figure 4-36(a) and (b). In melt pools with low boron concentration, solidification begins at the boundaries of the melt pool, causing boron to be rejected into the remaining liquid and increasing its concentration. In regions where the boron content exceeds the eutectic composition, TiB tends to precipitate preferentially during solidification (Figure 4-36(c)), followed by the precipitation of the β -titanium phase (Figure 4-36(d)). As β grains continue to grow, TiB is pushed to the grain boundaries (Figure 4-36(e)), accumulating and distributing along these boundaries (Figure 4-36(f)). Consequently, variations in boron concentration within the melt pools affect the fluid dynamics during the solidification process, leading to the redistribution of TiB within the formed β -grains (Figure 4-36(g)).

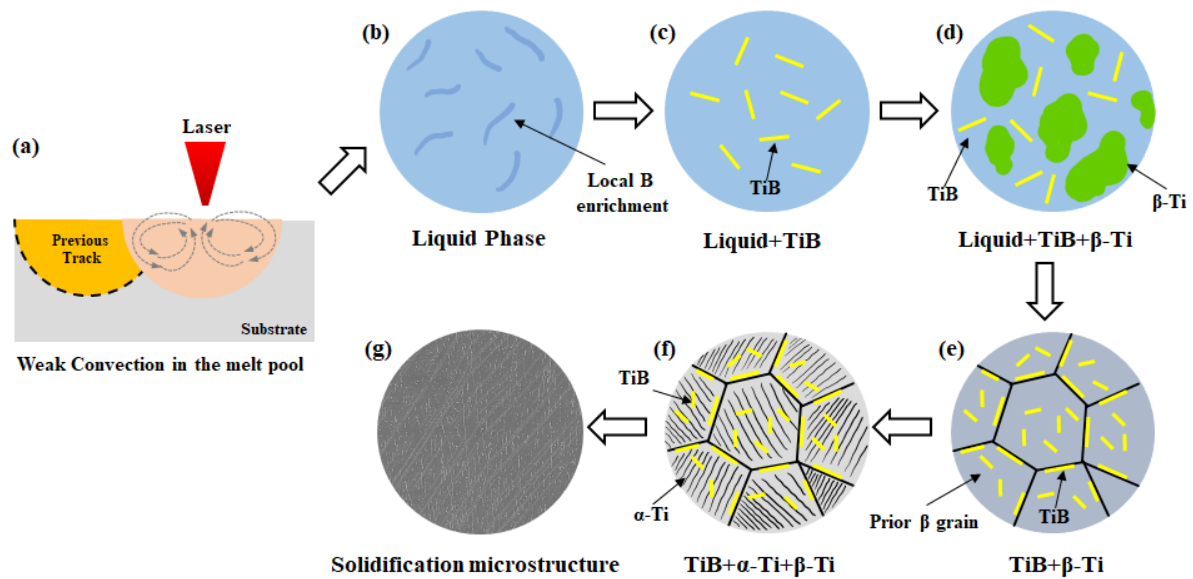


Figure 4-36 The schematic diagram illustrating solidification process of Ti6Al4V modified with a low concentration of boron during surface laser glazing procedure.

The high boron concentration in the Ti6Al4V-xB alloys induces strong convection within the laser micro-zone melt pool, as depicted in Figure 4-37(a), leading to a uniform distribution of boron on both macroscopic and microscopic scales (Figure 4-37(b)). This uniformity is attributed to the vigorous convection in the melt pool. Solidification occurs within the hypoeutectic range, where the prior β -titanium phase nucleates and grows first in the liquid phase (Figure 4-37(c)). The rapid non-equilibrium solidification, coupled with constitutional undercooling, leads to solute partitioning, promoting the growth of β -Ti and boron segregation, which results in a cellular morphology (Figure 4-37(d)). Upon reaching the eutectic temperature during cooling, eutectic transformation occurs, and the eutectic mixture (β -titanium + TiB) begins to form in the remaining liquid phase. Due to the narrow solidification temperature range, both the eutectic component content and TiB size are restricted (Figure 4-37(e)). As solidification continues and the temperature drops below the β to α phase transition temperature, the β -titanium phase transitions into the α phase (Figure 4-37(f)). In regions with elevated boron concentration, TiB structures develop into a quasi-continuous network microstructure, as shown in the room temperature microstructure (Figure 4-37(g)). Additionally, the needle-like or whisker-like B27 structure of TiB, characterized by its high specific surface area, leads to the alignment and aggregation of TiB whiskers during formation (Feng, Zhou, Jia, Meng, et al., 2006; W. Lu et al., 2001), especially in areas with higher boron content, resulting in the formation of a quasi-continuous network structure.

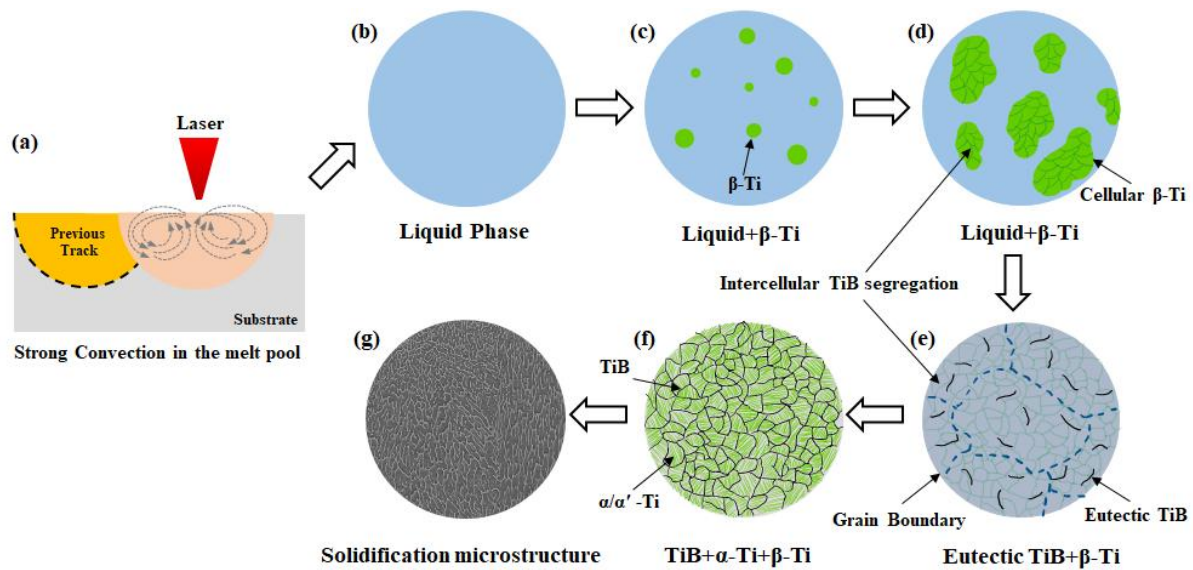


Figure 4-37 The schematic diagram illustrating solidification process of Ti6Al4V modified with a high concentration of boron during surface laser glazing procedure.

4.6 Conclusion

The addition of trace boron effectively promotes grain refinement and facilitates the columnar-to-equiaxed transition in Ti6Al4V alloys via formation of TiB phases, which significantly enhance hardness, wear resistance, and oxidation resistance. This strategy effectively addresses the epitaxial growth commonly observed in PBF-LB/M titanium parts while complying with strict chemical standards at minimal boron concentrations. In this study, arc melting and powder-free laser glazing were utilized to investigate boron additions ranging from 0.1 to 2.5 wt.% under rapid solidification conditions analogous to the PBF-LB/M process. The key findings include:

- Boron additions dramatically refined prior- β grain and α -colony structures, eliminating continuous grain boundary α networks. A minimal addition (~ 0.1 wt.%B) reduced grain sizes by approximately tenfold, with negligible further refinement above 0.2 wt.%B.
- Increased boron content consistently elevated hardness and elastic modulus due to grain refinement and hard TiB phase formation. Each additional 1 wt.% boron increased hardness by ~ 39 HV (from 356 HV at 0 wt.% to 492 HV at 2.5 wt.%). A distinctive “necklace” TiB microstructure formed at higher boron contents, further increasing stiffness.
- XRD analysis revealed that boron additions produced TiB (B27 orthorhombic) phases, retained β -titanium, redistributed α/α' intensities, and resulted in smaller crystallite sizes and more random orientations, without significant lattice distortions.
- EBSD analysis showed significant grain refinement and reduced texture intensity/index with increasing boron content, with Ti6Al4V-2.5B exhibiting the finest, most equiaxed grain structure.

- Laser glazing demonstrated that nanohardness and modulus increased linearly with boron content (from 3.65 GPa and 99 GPa at 0 wt.%B to 6.82 GPa and 138 GPa at 2.5 wt.%B), attributed to nanoscale TiB particles and grain refinement.
- Melt pool depth increased with boron addition due to exothermic TiB particle formation.
- Laser-glazed layers uniformly consisted of martensitic α' and TiB phases without β -phase retention, with TiB particles restricting grain growth and serving as nucleation sites.
- Effective microstructural refinement was achieved at boron contents ≥ 0.2 wt.%, above which quasi-continuous TiB networks formed, significantly enhancing properties under rapid solidification conditions.
- Increased laser exposure time reduced hardness and modulus in unmodified Ti6Al4V due to martensite coarsening but improved these properties in the boron-modified alloy (Ti6Al4V-0.1B), resulting from refined α' martensite and nanoscale TiB precipitates. Increased exposure times also resulted in deeper melt pools, particularly in boron-containing alloys.
- Surface XRD of laser-glazed alloys predominantly indicated martensitic α' formation, with internal stresses and microstructural refinement influenced by laser exposure. SEM-BSE imaging confirmed refined martensitic morphologies and nanoscale TiB precipitates in boron-modified alloys at longer exposures.
- EBSD analyses of laser-glazed surfaces confirmed that significant grain refinement occurred only in boron-modified alloys (Ti6Al4V-0.1B) at increased exposure durations (120 μ s), highlighting boron's critical role in promoting uniform and refined microstructures.

CHAPTER 5

COMPOSITE POWDER PRODUCTION AND CHARACTERIZATION

5.1 Introduction

Mechanical alloying, also known as dry powder coating, is an innovative and a completely solid-state technique that modifies surface properties and/or synthesizes novel alloys by applying smaller guest particles onto larger host particle surfaces (Pfeffer et al., 2001; J. Yang et al., 2005). This method contrasts with wet powder coating by directly manipulating micron-sized host particles with submicron-sized guest particles, thereby forming composite materials of higher functional value (Alonso & Alguacil, 1999.; Hersey, 1975). Unlike wet powder coating, mechanical alloying facilitates direct contact between guest and host particles through mechanical forces. The attachment of smaller guest particles to host particles is predominantly influenced by van der Waals forces, where initially agglomerated guest particle clusters adhere to host surfaces. Further particle interactions during mechanical mixing redistribute and disperse the guest particles, effectively coating the host particle surfaces (Dave et al., 2003; Pfeffer et al., 2001; J. Yang et al., 2005). The final coating, whether discrete or continuous, depends on factors such as the processing duration, the guest-to-host particle weight ratio, and the intrinsic properties of the particles involved. Continuous coating in dry powder coating processes may demonstrate as a porous particle layer, ranging from a monolayer to a multilayer structure, or as a non-porous continuous film. While continuous coatings are often preferred for their uniform coverage, the capacity to create discrete coatings is advantageous in applications requiring surface property modifications without full encapsulation of the underlying particle (Pfeffer et al., 2001). This coating technique not only positions guest particles in proximity to the host surfaces but may also cause guest particle deformation or embedment. Dry particle coating stands out as a versatile technique that significantly alters the properties and functionality of host particles, creating engineered particulates with tailored characteristics. Enhanced or modified properties include flowability, dispersibility, and solubility (Pfeffer et al., 2001). This versatility opens broad research possibilities and applications. Additionally, dry coating offers economic benefits by minimizing the use of costly or scarce materials, effectively applying a more valuable material (guest) onto a less expensive one (host). Moreover, it is environmentally beneficial, avoiding the generation of organic or aqueous waste associated with wet coating processes, thus offering an eco-friendly alternative.

In the following sections, this research examines the properties of composite powders to understand the mechanics and efficacy of the dry powder coating process. An energy-based stick-bounce approach provides the theoretical framework, analysing particle interactions to calculate adhesion energy, collision kinetic energy, plastic deformation energy, and deagglomeration energy. These calculations consider the sizes and material properties of both host and guest particles. Experimentally, this study employs the high-intensity vibrational LabRAM mixer. The research explores the impact of material stiffness and particle sizes, alongside process intensity, on coating quality. Additionally, two metrics are introduced for evaluation: the quality index of dry coating (K_c), which assesses coating performance, and the deagglomeration index (K_d), which measures the propensity for guest particle agglomeration. The findings from these analyses aim to enhance our understanding of the dry coating process, particularly in producing composite powders suitable for PBF-LB/M applications.

5.2 Theoretical

Previous research has shown both energy-based and momentum-based stick/bounce models can accurately predict sticking or bouncing behaviours after collisions occurring in dry coating (Almohammed & Breuer, 2016). In this thesis, the energy-based model is employed to examine the conditions of powder mixing. According to this model, the initial relative kinetic energy of colliding particles decreases to zero, converting into stored elastic energy. This energy then transforms back into kinetic energy, propelling the particles apart with less energy than initially due to energy dissipated during particle plastic deformation and other losses. Critically, some of this kinetic energy dissipates during deagglomeration, which must be incorporated into the model (Dave et al., 2003). As a result, the final relative kinetic energy is invariably lower than the initial. If this remaining energy exceeds the total detachment energy—including van der Waals energy, plastic deformation energy, and deagglomeration energy—the guest particle will rebound from the host. Otherwise, they will adhere. Energy losses occur through dissipation during coating, deagglomeration, and conversion of kinetic energy into heat. Hence, the model assumes that dissipated energy is absorbed by particle deformation. Additionally, since successful coating presupposes deagglomeration, the energy required to break apart agglomerations is factored into the total detachment energy. To assess the effectiveness of the dry coating process, a quality index of dry coating (K_c) is introduced. This index measures the ratio of relative kinetic energy to the combined detachment energies. The particulate materials considered here are modelled as idealized plastic spheres with uniform sizes and smooth surfaces, simplifying the analysis and interpretation of results.

5.2.1 Van der Waals Energy

To comprehensively understand the dry powder coating process, it is crucial to consider the inter-particle forces involved, such as van der Waals (vdW), electrostatic, and capillary forces (Israelachvili, 2011). In this context, vdW forces emerge as the dominant force, overshadowing the relatively weaker electrostatic and capillary forces (Castellanos, 2005). This thesis thus focuses primarily on van der Waals forces. As depicted in Figure 5-1, collisions between guest (fine) and host (coarse) particles result in their deformation. According to

Israelachvili (Israelachvili, 2011), the van der Waals energy (E_{vdW}) between macroscopic spheres can be calculated by summing up the energies from the areas of deformed surfaces in direct contact and those areas not in direct contact:

- i. E_{vdW} between two deformed surfaces (E_d) can be described as follows:

$$E_d = \frac{HS}{12\pi\delta^2} \quad 5.1$$

where H represents the *Hamaker* constant, S denotes the contact area between the two flat surfaces as defined in Equation 5.3, and δ is the atomic scale separation distance, typically assumed to be 0.165 nm.

- i. E_{vdW} between the rest of the surfaces of two spheres (E_s) is calculated by:

$$E_s = \frac{H}{6\delta} \frac{r_h r_g}{r_h + r_g} \quad 5.2$$

where the radii of host and guest particles are denoted as r_h and r_g , respectively.

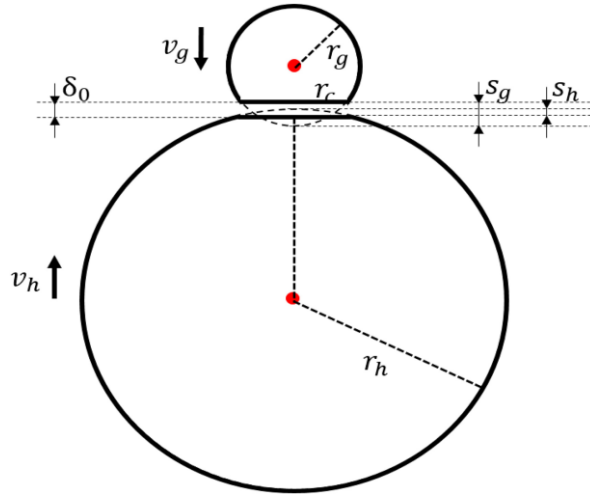


Figure 5-1 Schematic view of deformed particles in contact (Zheng et al., 2020).

As depicted in Figure 5-1, the formula to determine the contact surface area between two deformed particles is outlined as follows:

$$S = \pi r_c^2 \quad 5.3$$

where r_c represents the contact radius. Based on the Hertzian contact model (Johnson, 1987), r_c is defined as follows:

$$r_c = \left(\frac{3F \left(\frac{1-\nu_h^2}{E_h} + \frac{1-\nu_g^2}{E_g} \right)}{4 \left(\frac{1}{r_h} + \frac{1}{r_g} \right)} \right)^{1/3} \quad 5.4$$

where ν_h and ν_g are the Poisson's ratios of the host and guest particles, respectively, and E_h and E_g are the Young's moduli of the host and guest particles, respectively. F represents the contact force between the fine and coarse particles, which can be estimated as follows:

$$F = \frac{m\Delta v}{t} \quad 5.5$$

where m denotes relative mass, given in Equation 5.10, Δv represents relative velocity change before and after the collision, and t is the collision time to be estimated as (Patrício, 2022):

$$t = 2.86 \left(\frac{m^2 \left(\frac{1-\nu_h^2}{E_h} + \frac{1-\nu_g^2}{E_g} \right)^2}{\frac{r_h r_g}{r_h + r_g} v} \right)^{1/5} \quad 5.6$$

By substituting Equation 5.3 into Equation 5.1, E_d can be reformulated as follows:

$$E_d = \frac{Hr_c^2}{12\delta^2} \quad 5.7$$

Therefore, the van der Waals energy (E_{vdW}) between two deformed particles can be expressed as follows:

$$E_{vdW} = \frac{Hr_c^2}{12\delta^2} + \frac{H}{6\delta} \frac{r_h r_g}{r_h + r_g} \quad 5.8$$

5.2.2 Relative Kinetic Energy

Relative kinetic energy (E_{kin}) can be expressed as:

$$E_{kin} = \frac{1}{2} m v^2 \quad 5.9$$

where m represents the relative mass, and formulated as follows:

$$m = \frac{m_h m_g}{m_h + m_g} \quad 5.10$$

In above equations, m_h and m_g represent the masses of host and guest particles, respectively, while v denotes the relative velocity in Equation 5.9. The Resonant Acoustic® Mixer

(LabRAM) system, which operates on simple harmonic motion, allows particles to collide as they rebound from container walls. Thus, a basic estimate of average relative velocity is:

$$v = 2f \int_0^{\frac{1}{2f}} -\omega A \sin(\omega t) dt = 4Af \quad 5.11$$

where f signifies the frequency, set at 60 Hz in the LabRAM system, while ω represents the angular velocity. The amplitude of the vibration, A , depends on the load and intensity and can be experimentally determined using a slow-motion camera. Additionally, the dry coating process might be computationally simulated using the discrete element method (DEM), an approach that is well-suited for calculating such parameters and could be further explored in future studies. The behaviour of the tri-dimensional Turbula® mixer is complex and nearly chaotic. The particles experience a wide range of forces and velocities, varying in direction and amplitude, influenced by their positions within the powder bed and factors such as the rotational speed and size of mixer. Therefore, a basic estimate of the average relative velocity is given as (Mayer-Laigle et al., 2020):

$$v = 1.68 \times 10^{-2} (N) \quad 5.12$$

where N represents the engine speed of the rotary axis, expressed in revolutions per minute (rpm).

5.2.3 Plastic Deformation Energy

The energy required for plastic deformation (E_p) can be expressed as (K. Wang et al., 2008):

$$E_p = F \Delta s = F(s_g + s_h) \quad 5.13$$

where s_g and s_h denote the indentation depths of guest and host particles, respectively (refer to Figure 5-1), and F is the contact force calculated using Equation 5.5. Additionally, Equation 5.3 is expressed as follows:

$$S = \pi \left[r_g^2 + (r_g - s_g)^2 \right] = 2\pi r_g s_g - \pi s_g^2 = 2\pi r_h s_h - \pi s_h^2 \quad 5.14$$

Assuming that the contact radii of host and guest particles are significantly larger than their respective indentation depths ($r_g \gg s_g$ and $r_h \gg s_h$), the contact area between two deformed particles can be calculated as follows:

$$S \approx 2\pi r_g s_g \approx 2\pi r_h s_h \quad 5.15$$

Utilizing Equation 5.15, the extent of plastic deformation in the coarse particles can be calculated as follows:

$$s_h = \frac{r_g}{r_h} s_g \quad 5.16$$

Using Equations. 5.3 and 5.15, the depth of plastic deformation for fine particles can be computed as follows:

$$s_g = \frac{r_c^2}{2r_g} \quad 5.17$$

As $r_h \gg r_g$, according to Equation 5.16, $s_g \gg s_h$. Therefore, Equation 5.13 can be reformulated as:

$$E_p = Fs_g = \frac{Fr_c^2}{2r_g} \quad 5.18$$

5.2.4 Deagglomeration energy

In the dry coating process, the initial step involves large agglomerates of guest particles adhering to host surfaces, resulting in uneven coatings. Uniformity is achieved as particles repeatedly collide with each other and with system components like vessel walls, facilitating deagglomeration (Dave et al., 2003). During this phase, some guest particles detach from the agglomerates. The success of deagglomeration depends on whether the relative kinetic energy exceeds the deagglomeration energy, which causes guest agglomerates to break apart and disperse onto host particles. If the kinetic energy is insufficient, the guest particles remain clumped together. The energy needed for deagglomeration includes van der Waals (vdW) energy and energy from plastic deformation. Initially, to simplify calculations, interactions between just two guest particles can be considered. Therefore, Equation 5.8 is adapted by substituting the host particle size with that of the guest particle. The formula for deagglomeration energy (E_{de}) is as follows:

$$E_{de} = \frac{Hr_c^2}{12\delta^2} + \frac{Hr_g}{12\delta} + \frac{Fr_c^2}{2r_g} \quad 5.19$$

5.2.5 Determining Guest Attachment and Deagglomeration Energies

The total energy required for particle detachment encompasses van der Waals (vdW) energy, plastic deformation energy, and deagglomeration energy. If this total detachment energy exceeds the relative kinetic energy, the guest and host particles will adhere. However, if the relative kinetic energy is greater, the guest particles will rebound off the host particles (Almohammed & Breuer, 2016). To assess the quality of the dry powder coating, Equations 5.8, 5.9, 5.18, and 5.19 are used. It is also advantageous to define the quality index of dry powder coating (K_c), which is the ratio of total detachment energy to kinetic energy, as follows:

$$K_c = \frac{E_{vdW} + E_p + E_{de}}{E_{kin}} \quad 5.20$$

When $K_c > 1$, guest particles are more likely to adhere to the host particles; conversely, when $0 < K_c < 1$, there is a greater likelihood for the particles to separate. Furthermore, the quality index for deagglomeration (K_d) is defined as follows:

$$K_d = \frac{E_{de}}{E_{kin}} \quad 5.21$$

When $K_d > 1$, guest particle agglomerates are prone to further agglomeration, while if $0 < K_d < 1$, there is a higher likelihood of effective dispersion of guest particles.

5.3 Optimizing RAM Process for Composite Powder Production

5.3.1 Plastic Deformation and Phase Formation

The XRD patterns presented in Figure 5-2 compare the phase composition of raw powders and its Boron nanoparticles-decorated counterparts processed under a 10-minute RAM process at different gravitational accelerations. The characteristic peaks of α' -titanium phase were prominently identified in all samples, as denoted by the diamond symbols. Additionally, the presence of TiO_2 was detected, indicated by the inverted triangle symbols, across the samples. The Rietveld analysis on the host powder exhibited a TiO_2 of approximately 7% by weight. After the application of the RAM process, starting at 10G and extending up to 100G, there was a notable decrease in the volume fraction of TiO_2 , stabilizing at around 3% across all processed samples. This finding demonstrated the effectiveness of the RAM process in altering the oxide phase composition within the powders. This reduction aligns with studies where mechanical treatments, such as ball milling, diminish oxide layers through repetitive fracturing and welding (Suryanarayana, 2001). Furthermore, the analysis revealed an increase in microstrain from the 10G to 100G samples, as evidenced by the progressive broadening of the diffraction peaks. This peak broadening suggested a manifestation of lattice distortions, commonly associated with the introduction of mechanical stresses during processing (Hull & Bacon, 2011). The observed gradual increase in broadening with the applied G-force implied the mechanical energy imparted by the RAM process contributed to strain within the crystalline structure of the powders, affecting both the microstructure and the phase composition.

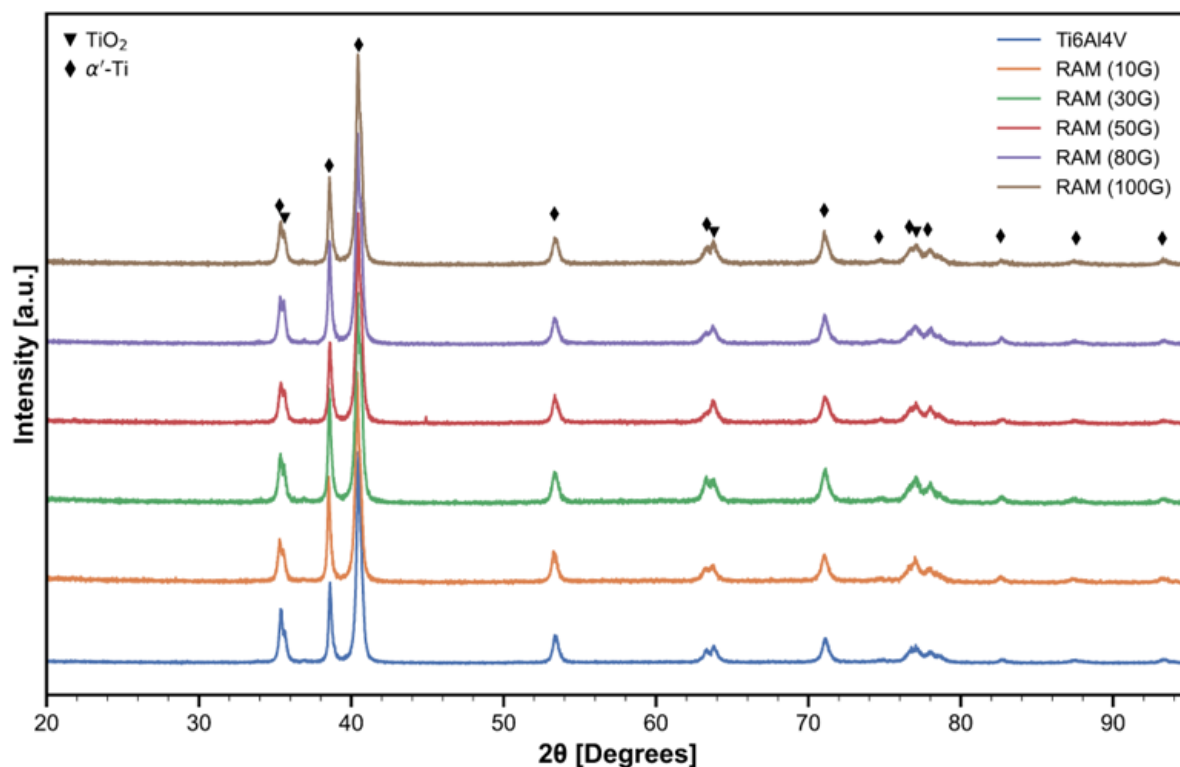


Figure 5-2 Comparative X-ray diffraction patterns of 0.1 wt.%B nanoparticle-decorated Ti6Al4V powder under 10-minute RAM process at different gravitational accelerations.

Figure 5-3 provides a comparative analysis of the microstrain and crystallite size in Boron nanoparticle-decorated Ti6Al4V powder particles, which were subjected to a 10-minute RAM process at various gravitational accelerations. The host powder exhibited a microstrain of 6.53×10^{-3} and a crystallite size of 79.62 nm. Post-RAM processing at 10G, the microstrain slightly increased to 6.72×10^{-3} and the crystallite size decreased to 59.32nm. At 30G, the microstrain continued to rise to 7.05×10^{-3} , with a corresponding decrease in crystallite size to 57.92nm. This trend of increasing microstrain with concurrent reduction in crystallite size was observed to continue at 50G, reaching a microstrain of 7.31×10^{-3} and a crystallite size of 54.03nm. However, at 80G applied force, a notable deviation occurred; the microstrain significantly increased to 7.60×10^{-3} , and the crystallite size was substantially reduced to 48.94nm, indicating a considerable impact of the higher G-forces on the powder structure. At the highest gravity of 100G, the microstrain further escalated to 8.01×10^{-3} , while the crystallite size showed a slight increase to 56.37nm, potentially due to dynamic recovery or partial recrystallisation at extreme mechanical energies (Humphreys, 2004). The results explicitly indicated that a clear increase in microstrain was observed with rising gravitational forces, from 6.53×10^{-3} at the host powder to 8.01×10^{-3} at composite powder subjected to 100G-gravitational force. Concurrently, the crystallite size displayed a general trend of reduction from 79.62nm in the raw material to 48.94nm at 80G, followed by a slight increase to 56.37nm at 100G. The inverse correlation between microstrain and crystallite size underscores the role of dislocation accumulation in grain refinement during high-energy processing (Hansen et al., 2001).

Although crystallite size estimations can be performed using the Scherrer equation, it inherently assumes that peak broadening originates solely from finite crystallite size and disregards the influence of microstrain, instrumental broadening, and potential lattice defects. Moreover, the Scherrer approach typically presumes spherical crystallite shapes, which may not accurately represent the true morphology. These simplifications often lead to over- or under-estimation of crystallite sizes, particularly when samples exhibit significant strain or other sources of peak broadening. To circumvent these limitations, this study employed Rietveld refinement, which accommodates both microstrain and crystallite size simultaneously while also accounting for additional parameters such as preferred orientation, lattice distortions, and instrument-specific effects (Rietveld, 1969; Scherrer, n.d.). Consequently, the observed trend of increasing microstrain alongside overall crystallite size reduction—with a slight crystallite size rebound at the highest G-force—has been more accurately characterized by Rietveld analysis, offering a robust and reliable insight into the evolution of microstructural features under escalating gravitational forces.

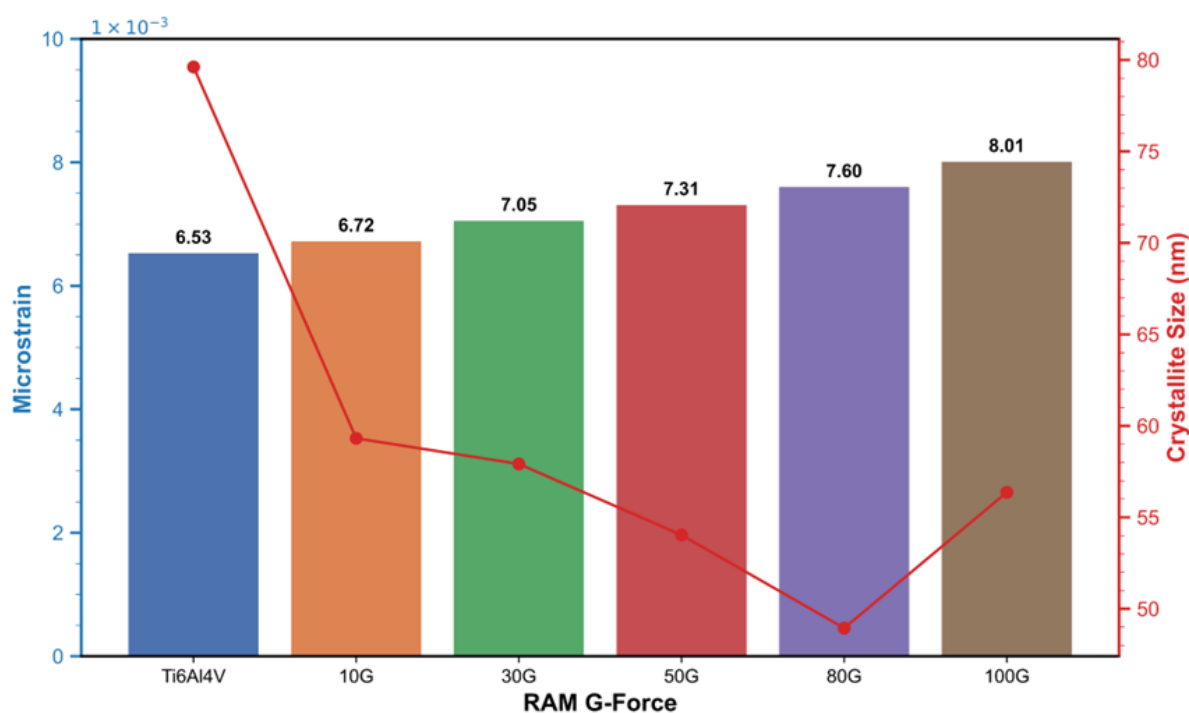


Figure 5-3 Comparative of microstrain and crystallite size of 0.1 wt.%B nanoparticle-decorated Ti6Al4V powder under 10-minute RAM process at different gravitational accelerations.

Figure 5-4 displays XPS spectra comparing raw powder to 0.1 wt% Boron-decorated samples under different RAM processing intensities. The as-received Ti6Al4V powder showed surface peaks for the elements expected from its native oxide and contaminant layer: primarily titanium and oxygen from TiO_2 , aluminium, and smaller signals from carbon (adventitious hydrocarbon), nitrogen, and a trace of silicon. This is consistent with the naturally oxidised state of Ti6Al4V powder, which typically forms a TiO_2 -rich surface with minor Al_2O_3 ; vanadium is

usually present only in small amounts as V_2O_5 or not detected at all due to the overlying oxides (Neacsu et al., 2020). After RAM coating with boron at 10G and 30G, new peaks corresponding to boron (B1s) and its oxide (B_2O_3) appeared in the spectra, in addition to all the original elements seen in the host particles. The detection of boron in the 188–192 eV range (B1s region) alongside signals for B–O bonding confirms that boron nanoparticles were successfully deposited onto the Ti6Al4V powder surface, and some of this boron is present in oxidised form (Jung et al., 2016). This agrees with reports that boron is readily oxidised to B_2O_3 when exposed to air or during milling, producing a surface boron-oxide layer (Jung et al., 2016). The presence of B_2O_3 here indicates that the boron additives either carried a native oxide or became partially oxidised during RAM processing. At higher RAM intensities of 50G, 80G, 100G, the XPS survey spectra continued to show B and B_2O_3 peaks, confirming the persistent coating of boron/boron-oxide on the powder. Additionally, a vanadium (V2p) signal emerges at these higher G-forces (50G and above), although it remains relatively minor compared to the dominant Ti and O peaks. The appearance of a detectable V peak suggests that the more energetic RAM conditions may have caused slight abrasion or mixing of the surface, enough to expose some vanadium at the outermost surface or in an oxidised state. This is noteworthy because in the baseline powder the vanadium was either not observed or extremely faint due to it being buried under oxides. Its presence after intense RAM implies a more complex surface modification at higher gravitational accelerations, possibly involving the disruption of the passive oxide layer and exposure of the underlying alloy constituents (Suryanarayana, 2001). In summary, the XPS results from Figure 5-4 demonstrate that increasing RAM intensity leads to progressively enriched surface chemistry: first with boron and boron oxide species at low G, and then with trace vanadium from the substrate alloy at the highest G levels.

These surface chemistry modifications could be significant for powder performance in additive manufacturing. The incorporation of boron on the surface may influence oxidation resistance or act as a gettering layer, and the slight reduction of TiO_2 coverage might affect how the powder interacts with a laser beam in PBF-LB/M processes. For instance, different oxide layers can alter optical absorption or wetting behaviour of a powder during melting (Suryanarayana, 2001). Thus, the RAM process not only tailors the bulk microstructure (as shown by XRD) but also tunes the surface composition of the powder. The results presented in Figure 5-2 – Figure 5-4 provide a comprehensive picture of these effects: RAM-driven acoustic energy at 10G – 100G can effectively reduce surface oxides, induce lattice strain (distortions) in the α' -Ti lattice, refine crystallite size, and deposit nanoparticulate additives (boron) onto powder surfaces. All these changes are expected to play a role in the subsequent powder bed fusion process and final build properties, underscoring the importance of controlled powder mixing parameters in powder metallurgy and additive manufacturing (Al-Joubori et al., n.d.; Begum et al., 2012).

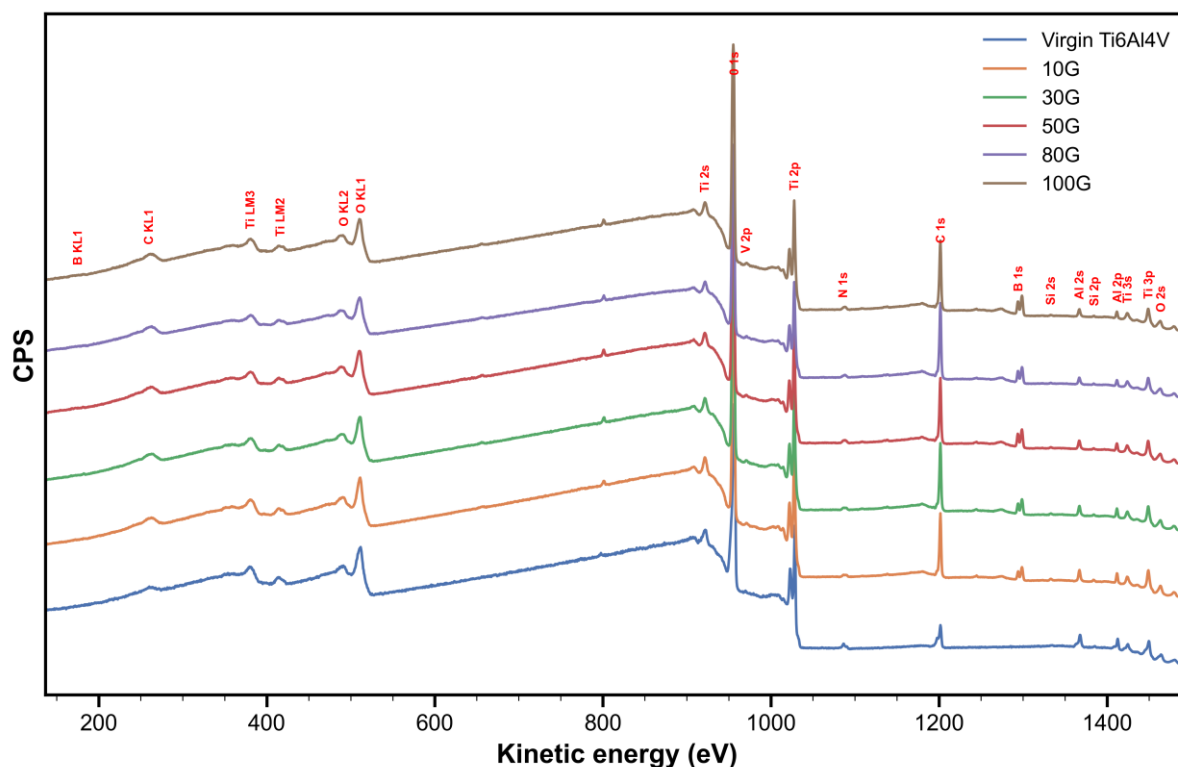


Figure 5-4 Comparative XPS Survey spectra of raw and 0.1 wt.%B nanoparticle-decorated powder under 10-minute RAM process at different gravitational accelerations.

5.3.2 Powder Morphology and Particle Size Distribution

The SEM micrographs in Figure 5-5 present a comparative study of host powder in both its raw form and 0.1 wt% Boron nanoparticle-decorated powder under 10-minute RAM process at different acceleration gravities. The micrographs depicted the morphological changes under varying conditions of acceleration gravity ranging from 10G to 100G, over a consistent mixing of 10-minute. The orange ellipses in Figure 5-5 highlighted free guest particles, indicating those not adhered to the host powder, while the red arrows in subsequent micrographs demonstrated an increasing number of guest particles bonding to the host. Initially, the host powder (Figure 5-5(a)) displayed a clean, spherical morphology, serving as the baseline for comparison. As the acceleration gravity was increased from 10G (Figure 5-5(b)) to 100G (Figure 5-5(f)), a trend of guest particles adhering to the host was observed. Contrary to the anticipated increase in guest particle adhesion, the micrographs Figure 5-5(b) through Figure 5-5(f) suggested a paradoxical reduction in adhered guest particles at higher accelerations. This suggests a threshold beyond which kinetic energy imparted to the particles exceeds interfacial adhesive forces, leading to detachment—a phenomenon consistent with the Hertzian impact theory, where excessive collision energy disrupts particle cohesion (Johnson, 1987b; Rojac & Kosec, 2010). The absence of a continuous boron nanoparticle coating layer at higher G-forces (seen in Figure 5-5(e) and (f)) may arise from two factors: (i) insufficient plastic deformation of the host powder to anchor nanoparticles under extreme accelerations, or (ii) a coating thickness below

the lateral resolution limit of SEM which is around 5 nm for secondary electron imaging under the applied conditions (Goldstein et al., 2017). The latter hypothesis aligns with EDS data, which detected boron signatures even at 100G, implying sub-resolution surface modifications. These observations underscore the delicate balance between mechanical energy input and interfacial adhesion in nanoparticle decoration processes, as reported in mechanochemical surface engineering studies (Agarwal et al., 2021; Baláz et al., 2014). Critically, the apparent "bouncing effect" at 100G (Figure 5-5(f)) challenges conventional assumptions that higher G-forces universally enhance particle adhesion. This behaviour mirrors findings in high-velocity cold spray processes, where excessive impact velocities reduce deposition efficiency due to particle rebound (Assadi et al., 2003). Such non-linear adhesion dynamics necessitate optimisation of RAM parameters to maximise nanoparticle retention while mitigating energy-induced detachment—a key consideration for functionalised additive manufacturing powders requiring uniform surface modifications (I. Gibson et al., 2020).

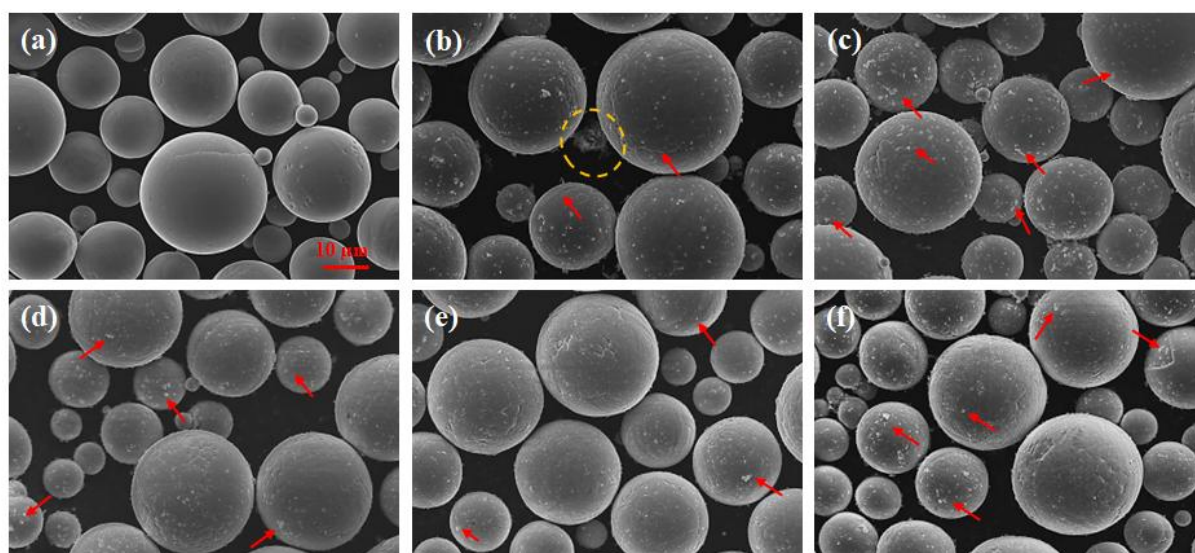


Figure 5-5 SEM (SE) micrographs of (a) raw Ti6Al4V powder; and 0.1 wt.%B modified powder under 10-minute RAM Mixing process at the acceleration gravity of (b) 10G; (c) 30G; (d) 50G; (e) 80G and (f) 100G. The orange ellipses in (b) indicate the free guest particles not attached to host powder, while red arrows indicate attached guest particles.

Figure 5-6 presents SEM images and EDX elemental maps delineating the distribution of boron nanoparticles within a host powder matrix after a 10-minute RAM mixing process at varying gravitational forces. The SEM images illustrated the powder morphology without providing clear evidence of boron presence due to the scale of resolution. However, the EDX maps for titanium and boron, depicted in the middle and bottom rows, offered a quantitative assessment of boron distribution. At 10G acceleration gravity, boron detection was minimal, suggesting an insufficient interaction between guest and host particles. Progressing to higher G-forces, the EDX maps displayed an increased guest presence, with the maximum signal intensity observed at 80G, indicating the most effective boron decoration at this condition. Beyond this point, at

100G, there was a notable decrease in the Boron signal. This could indicate a reduction in adherence of nanoparticles to the host surface or possible dispersion, as higher gravitational forces could cause the guest particles to rebound from the powder surface. These results demonstrated that guest decoration on host powder was not linearly proportional to the applied G-forces. There was a marked peak in guest adherence at 80G, represented an optimal point for nanoparticle-decoration before the efficiency diminished at higher acceleration gravities.

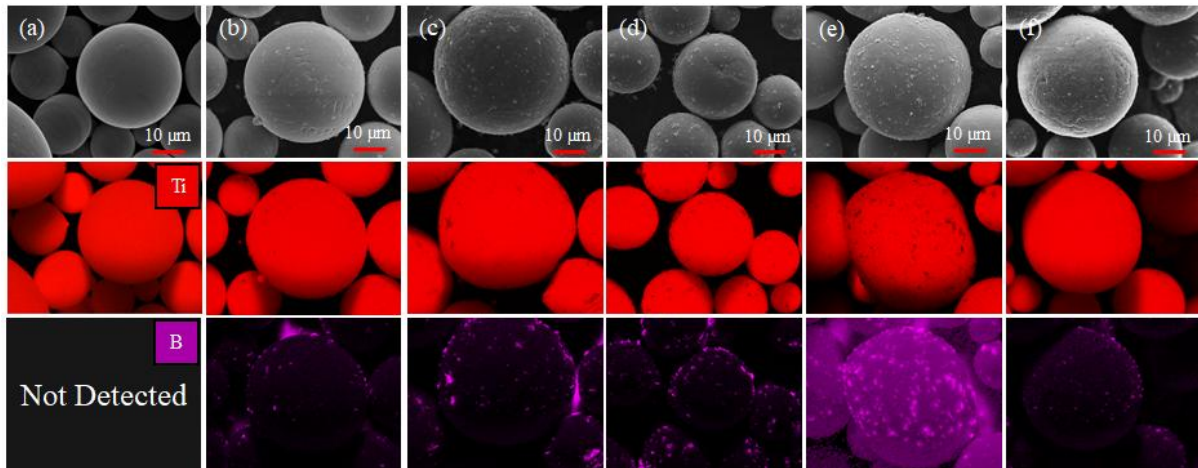


Figure 5-6 SEM (SE) images (top) of the composite powder and EDX elemental maps of Ti (middle) and B (bottom) for (a) raw Ti6Al4V powder; composite powders after 10-minute RAM Mixing process at the acceleration gravity of (b) 10G; (c) 30G; (d) 50G; (e) 80G and (f) 100G.

Figure 5-7 highlights the particle size distribution of raw powder compared to that of Boron nanoparticle-decorated powder after undergoing various 10-minute RAM processes at different acceleration gravity forces. Across all the samples, the peak volume density was consistently observed around 33μm, indicating a central tendency in particle size irrespective of the applied G-force intensity. For the sample mixed at 10G, in addition to the main peak at 33μm, there was a secondary, smaller peak present at lower particle sizes. This secondary peak could be indicative of a fraction of the powder mixture that possibly remained unattached, resulting in a bimodal distribution where a subset of particles was significantly smaller than the primary powder population. This bimodality mirrors observations in low-energy mechanical mixing processes, where insufficient interfacial energy prevents guest particle retention (Gärtner et al., 2021). This presence of a bimodal size distribution was not evident in samples subjected to higher mixing forces (30G up to 100G), which instead displayed a monomodal peak pattern. The absence of peaks corresponding to lower particle sizes in the samples subjected to higher mixing forces implies the successful attachment of guest nanoparticles to the host powder particles, resulting in a singular, more uniform distribution profile indicative of a homogenous mixture (Kollo et al., 2010). Consequently, the results confirmed the mixing process at 10G was insufficient for achieving a homogeneous powder blend, as demonstrated by the bimodal distribution. In contrast, higher mixing forces effectively eliminated the presence of discrete,

smaller particle aggregates, achieving a more homogeneous particle size distribution as desired for subsequent material processing.

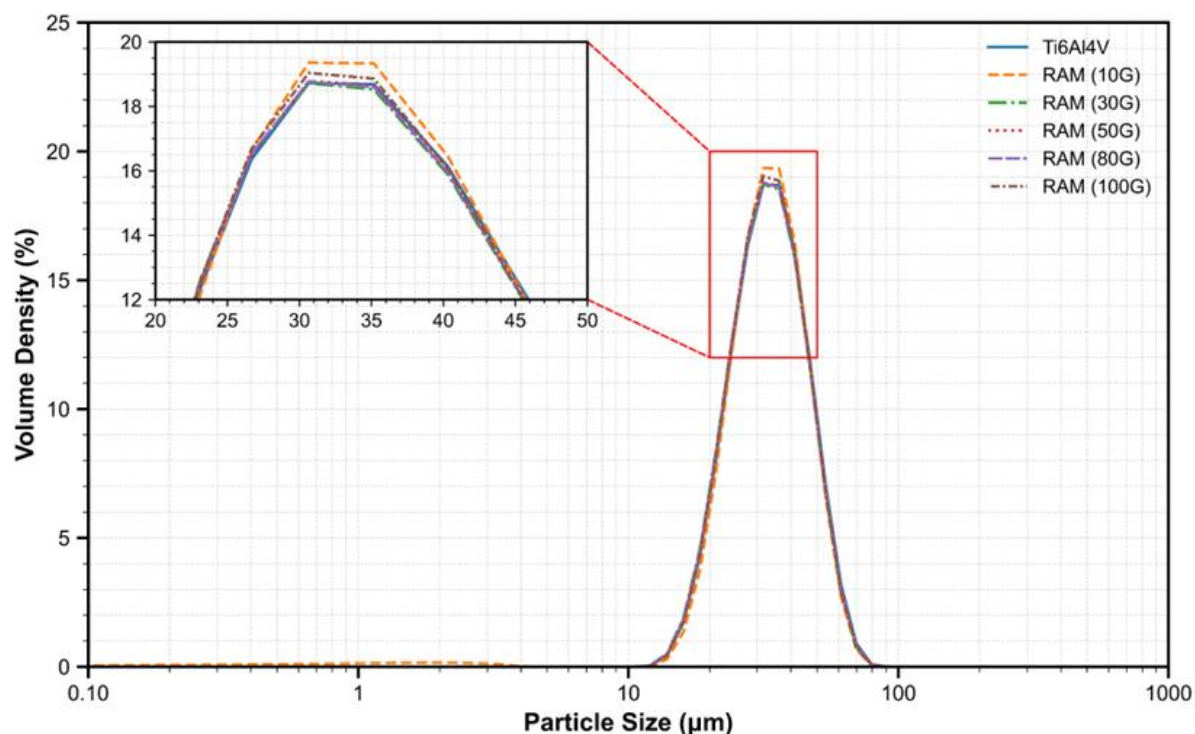


Figure 5-7 Evaluation of the powder size distribution of raw and 0.1 wt.%B nanoparticle-decorated Ti6Al4V powder mixtures after 10-minute RAM processes at different acceleration gravity forces.

The histogram and cumulative particle size distribution presented in Figure 5-8 illustrate the detailed analysis of alloy powder, both in its raw form and 0.1 wt% Boron nanoparticle-decorated powder under 10-minute RAM processes at different gravitational accelerations. The raw powder (Figure 5-8(a)) exhibited a median particle size (d_{50}) of 33.0 μm . The particle size analysis after introduction of guest nanoparticles and mixing at a 10G-force (Figure 5-8(b)) demonstrated a slight shift towards higher values in the d_{10} , d_{50} , and d_{90} measurements. These changes were attributed to the guest nanoparticles binding to the host powder particles, creating a 'decorative' effect on the surface. Additionally, the increased particle size parameters suggested that alongside the individual nanoparticles, there were aggregates of Boron present on the surface, influencing the overall increase in particle size distribution. This trend of increased particle size distribution values persisted across subsequent mixing conditions at 30G (Figure 5-8(c)), 50G (Figure 5-8(d)), 80G (Figure 5-8(e)), and 100G (Figure 5-8(f)), with the median particle size (d_{50}) consistently rising marginally above that of the raw material, indicating the presence of guest nanoparticles possibly contributing to an increase in the overall particle size. Despite the increase in size distribution values, the shape of the distribution curves suggested a maintained unimodality, with the d_{50} values indicating a median particle size for the composite powders at 33.4 μm for 10G, 33.6 μm for 30G, 33.7 μm for 50G, 33.9 μm for 80G,

and 33.5 μm for 100G. These values reflected the slight but consistent elevation compared to the raw powder. The histograms did not reveal significant bimodal distributions, which would have suggested uneven mixing. Instead, the relatively smooth and unimodal distribution patterns at higher G-forces implied a successful dispersion of guest nanoparticles throughout the host particle surface. The results, therefore, indicated that the addition of guest nanoparticles and the application of RAM Mixing at specified G-forces slightly enlarged the particle size of the powder while maintaining a homogeneous distribution, with no significant agglomeration that often accompanied the introduction of nanomaterials into metal powders.

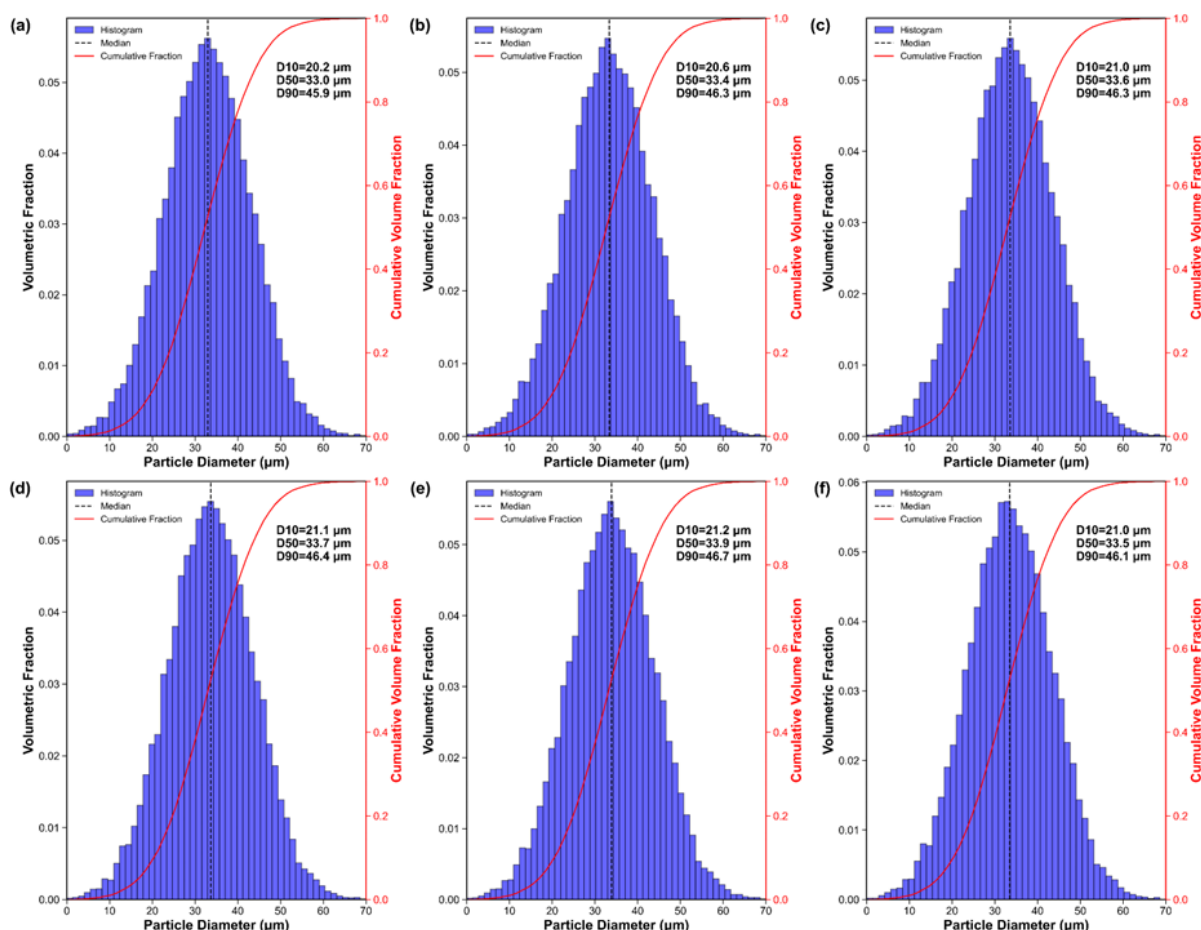


Figure 5-8 Histogram of the particle size distribution and cumulative particle size distribution of (a) raw Ti6Al4V powder; and 0.1 wt.%B modified Ti6Al4V powder under 10-minute RAM Mixing process at the acceleration gravity of (b) 10G; (c) 30G; (d) 50G; (e) 80G and (f) 100G.

Table 5-1 details the particle size distribution results for Ti6Al4V powder, both in its raw form and with 0.1 wt% Boron-decorated, processed using RAM at various gravitational forces. For the host powder, the particle size distribution is characterized by a d_{10} of 20.2 μm , d_{50} of 33.0 μm , and a d_{90} of 45.9 μm , with the span, a measure of the width of the particle size distribution, at 0.78. Upon 10-minute mixing at 10G, the d_{10} increases to 20.6 μm , the d_{50} to 33.4 μm , and the d_{90} to 46.3 μm . The span slightly decreased to 0.77, indicating a minor narrowing in size

distribution. When subjected to 30G-force, the d_{10} value slightly decreased to 21.0 μm , the d_{50} rose to 33.6 μm , and the d_{90} dropped to 46.3 μm , with the span further narrowing to 0.75, a more uniform distribution compared to the host powder. At 50G, the d_{10} slightly increased to 21.1 μm , the d_{50} remained consistent at 33.7 μm , and the d_{90} maintained at 46.4 μm . The span continued at 0.75, reflecting a stable particle size distribution despite increased gravitational forces. An 80G mixing resulted in a d_{10} of 21.2 μm , a d_{50} of 33.9 μm , and a d_{90} of 46.7 μm , with the span consistent at 0.75. Finally, at 100G, the d_{10} remained at 21.0 μm , the d_{50} at 33.5 μm , and the d_{90} slightly decreased to 46.1 μm , with the span holding steady at 0.75, suggesting that even at the highest gravitational forces, the powder maintains a similar size distribution to that seen at lower forces.

Table 5-1 The particle size distribution results presenting the cumulative distribution of d_{10} , d_{50} , and d_{90} as well as span for the raw and the 0.1 wt.%B nanoparticle-decorated Ti6Al4V powders under 10-minute RAM processes at different gravitational accelerations.

<i>Processing Method</i>	<i>d_{10} (μm)</i>	<i>d_{50} (μm)</i>	<i>d_{90} (μm)</i>	<i>Span ($\frac{d_{90} - d_{10}}{d_{50}}$)</i>
Raw Ti6Al4V	20.2 $\pm$ 0.185	33.0 $\pm$ 0.105	45.9 $\pm$ 0.104	0.78
10G Mixing Force	20.6 $\pm$ 0.015	33.4 $\pm$ 0.012	46.3 $\pm$ 0.040	0.77
30G Mixing Force	21.0 $\pm$ 0.002	33.6 $\pm$ 0.054	46.3 $\pm$ 0.047	0.75
50G Mixing Force	21.1 $\pm$ 0.020	33.7 $\pm$ 0.017	46.4 $\pm$ 0.015	0.75
80G Mixing Force	21.2 $\pm$ 0.027	33.9 $\pm$ 0.023	46.7 $\pm$ 0.013	0.75
100G Mixing Force	21.0 $\pm$ 0.019	33.5 $\pm$ 0.015	46.1 $\pm$ 0.012	0.75

5.3.3 Flow Properties of Composite Powders

Table 5-2 outlines the dynamic flow properties of Ti6Al4V powder, both raw and Boron-decorated, subjected to RAM processing at different gravitational accelerations. The basic flow energy for the host powder was measured at 13.861 mJ. After 10-minute mixing at 10G, BFE rose to 19.108 mJ, indicating reduced flowability due to initial nanoparticle adhesion-induced interlocking (Freeman, 2007). At 30G, BFE slightly decreased to 15.140 mJ, and this downward trend persisted at 50G and 80G, with BFE reaching 12.640 mJ and 12.103 mJ, respectively, suggesting progressive particle smoothing or fragmentation under higher mechanical forces, a phenomenon observed in mechanochemically processed powders (Suryanarayana, 2001). With the application of 100G-force, BFE experienced a minor increase to 12.278 mJ. The SI experienced a slight increase from 0.985 at host powder to 0.998 after 10G treatment and then gently fell, reaching 0.941 at 100G, indicating subtle variations in powder stability under pressure. FRI demonstrated relative steadiness, with a minor decrease from 1.303 in the host powder to approximately 1.234 post 10G RAM treatment, revealing consistent flow under varying forces. Specific energy initially rose from 0.501 mJ/g in the raw state to 0.685 mJ/g at 10G, then decreased to 0.441 mJ/g at 100G, reflecting the changing energy required for flow initiation due to the RAM process. Conditional bulk density displayed initial reduction from the raw 2.641 g/cm³ to 2.403 g/cm³ at 10G, likely due to nanoparticle-induced surface

roughness disrupting packing efficiency (Santomaso et al., n.d.). Subsequent density recovery of 2.660 g/cm³ at 80G aligns with particle rearrangement and attrition-driven size uniformity, enhancing packing dynamics at higher G-forces, and then marginally decreasing to 2.658 g/cm³ at 100G-force. These results in Table 5-2 illustrate the alterations in flow properties and densities of alloy powders as a consequence of 10-minute RAM processing, highlighting a general trend of reduced flow energy and bulk densities with varied gravitational forces applied during mixing.

Table 5-2 Comparison of the dynamic flow properties of raw and 0.1 wt.%B nanoparticle-decorated Ti6Al4V powders processed using different gravitational accelerations.

<i>Processing Method</i>	<i>BFE (mJ)</i>	<i>SI</i>	<i>FRI</i>	<i>SE (mJ/g)</i>	<i>CBD (g/cc)</i>
Raw Ti6Al4V	13.861	0.985	1.303	0.501	2.641
10G Mixing Force	19.108	0.998	1.234	0.685	2.403
30G Mixing Force	15.140	0.958	1.364	0.648	2.635
50G Mixing Force	12.640	0.946	1.333	0.485	2.645
80G Mixing Force	12.103	0.945	1.303	0.413	2.660
100G Mixing Force	12.278	0.941	1.318	0.441	2.653

In Figure 5-9, FFC is depicted for the host powder and Boron nanoparticle-decorated Ti6Al4V powder subjected to different gravitational accelerations during a 10-minute RAM process. The host powder sets a baseline FFC, against which the effects of RAM processing can be measured. The application of a 10G force during RAM processing resulted in an alteration of the FFC, suggestive of modified flow properties. With the increase in RAM processing force to 30G, 50G, 60G, 80G, and 100G, there was a discernible trend in the FFC values. The general increase in FFC across these samples was indicative of a progressive enhancement in the powder flowability. The FFC values peaked notably at the higher gravitational forces of 80G and 100G. This trend correlates with reduced cohesion and interparticulate friction, likely attributable to the mechanical smoothing of powder surfaces and disruption of agglomerates under high-energy impacts—a phenomenon documented in studies linking mechanical processing to flowability optimisation (Freeman, 2007). The pronounced FFC elevation at 80G and 100G underscores the role of gravitational acceleration in tailoring powder flow characteristics. Higher G-forces likely promoted more efficient energy transfer during collisions, mitigating adhesive van der Waals forces and surface asperities that dominate cohesion in fine powders (Seville et al., 2000). These findings align with empirical models where mechanical agitation reduces flow resistance by modifying surface topography and particle packing dynamics (Schulze, 2021). The results affirm that RAM processing parameters, particularly gravitational acceleration, critically influence the flow performance of Ti6Al4V-based powders, a vital consideration for additive manufacturing feedstock optimisation.

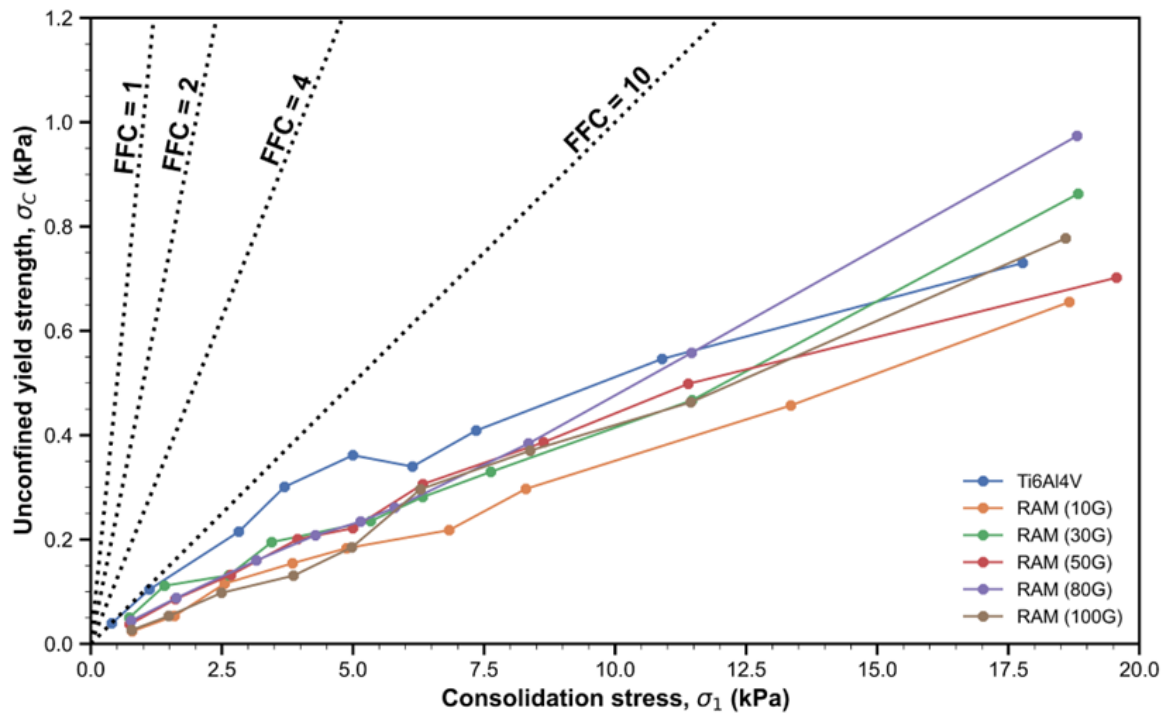


Figure 5-9 Flow functions of raw Ti6Al4V powder and 0.1 wt.%B nanoparticle-decorated Ti6Al4V powder subjected to 10-minute RAM processes at different gravitational accelerations.

Table 5-3 reports the average shear properties of raw and 0.1 wt% Boron nanoparticle-decorated powders after undergoing 10-minute RAM processing at various gravitational accelerations. The cohesion value for the host powder was 0.122 kPa, indicating the initial particle-to-particle adhesive force. After 10-minute mixing at 10G, the cohesion slightly increased to 0.130 kPa, suggesting that the RAM process may cause a mild increase in particle adhesion likely due to surface roughening or particle reshaping. When the gravitational force was increased to 30G, there was a slight decrease in cohesion to 0.113 kPa. This value decreased further at 50G, registering at 0.094 kPa, and at 80G, the cohesion dropped to 0.078 kPa. This trend suggested higher RAM forces could be contributing to a decrease in particle cohesion, potentially due to particle breakage or a reduction in the effective surface area for adhesion due to Boron nanoparticle decoration. However, at 100G, the cohesion increased again to 0.111 kPa. For the host powder, the angle of internal friction was measured at 16.469° and the flow function coefficient at 16.89. When the powder is subjected to a 10G RAM process, the AIF increases to 19.874° and the FFC decreases slightly to 14.83, indicating a change in the flow characteristics due to the mechanical forces applied. As the RAM force rises to 30G, there is a subtle decrease in AIF to 15.484° and an increase in FFC to 19.19. As the RAM gravitational forces increased, AIF generally decreased, reaching 14.423° at 50G, and 13.599° at 80G, respectively, while FFC increased, reaching 20.54 at 50G, and 24.99 at 80G, respectively, indicating changes in the powder flow characteristics likely due to the mechanical alterations from RAM processing. However, the 100G treatment resulted in a slight increase in AIF to 15.864° and an increase in FFC to 21.54. These results collectively suggested that RAM

processing influenced the shear properties of the host powder, with varying gravitational forces impacting cohesion, internal friction, and flow function of the powder.

Table 5-3 Average shear properties of raw and 0.1 wt.%B nanoparticle-decorated Ti6Al4V powders under 10-minute RAM processes at different gravitational accelerations.

<i>Processing Method</i>	<i>Cohesion (kPa)</i>	<i>AIF (°)</i>	<i>FFC</i>
Raw Ti6Al4V	0.122 ± 0.080	16.469 ± 1.726	16.89 ± 6.06
10G Mixing Force	0.130 ± 0.106	19.874 ± 1.645	14.83 ± 5.99
30G Mixing Force	0.113 ± 0.098	15.484 ± 1.645	19.19 ± 2.33
50G Mixing Force	0.094 ± 0.123	14.423 ± 2.085	20.54 ± 4.16
80G Mixing Force	0.078 ± 0.072	13.599 ± 2.171	24.99 ± 5.74
100G Mixing Force	0.111 ± 0.093	15.864 ± 2.634	21.54 ± 6.22

5.3.4 Laser Reflectivity Measurements

Figure 5-10(a) illustrates the reflectivity of raw and Boron-decorated powders subjected to RAM processes at varying gravitational accelerations, in line with established methodologies for measuring laser–powder interactions in PBF-LB/M studies (D. He et al., 2023). The unmodified Ti6Al4V powder exhibited a stable reflectivity of just below 40% at 1070nm, consistent with reported absorptivity values of approximately 60% for this alloy under fibre-laser irradiation (Alsaddah et al., 2022; R. Wang et al., 2022). Decorating the powder surface with boron under a low acceleration of 10G led to a modest reduction in reflectivity, signalling the initial adhesion of boron nanoparticles, which is known to enhance surface absorption by increasing roughness and introducing plasmonic scattering centres (Bidulsky et al., 2021; C. Ma et al., 2016). When the gravitational force was increased to 30G, reflectivity further decreased, indicating a greater transfer of boron onto the host particles and a corresponding amplification of photon trapping through multiple scattering (Boley et al., 2016; Tertuliano et al., 2024). Subsequent treatments at 50G and 80G yielded progressive reductions in reflectivity, underscoring the strong correlation between higher gravitational acceleration intensities, nanoparticle coverage, and surface morphology modifications that foster absorptivity (J. Sun et al., 2022; Tertuliano et al., 2024). However, at 100G, reflectivity partially rebounded to levels comparable to the 30G condition, a phenomenon attributable to the kinetic rebound of loosely bound particles under extreme acceleration, as observed in other high-energy particle impact studies (D. He et al., 2023; J. Sun et al., 2022). Figure 5-10(b) consolidates these measurements at 1070nm, demonstrating that RAM-induced surface modifications exert a pronounced influence on the optical coupling efficiency of feedstock powders during PBF-LB/M, with direct implications for energy absorption and subsequent component densification (Boley et al., 2016; Tertuliano et al., 2024). The host powder set a reference point with a reflectivity of 34.4% (Alsaddah et al., 2021; R. Wang et al., 2022). When subjected to a 10-minute mixing at 10G-force, the reflectivity decreased to 29.0%, which signifies the initial impact of the RAM treatment on the reflectivity. Increasing the RAM intensity to 30G caused a further decline in reflectivity, registering at 26.8%, demonstrating

continued surface changes with more intense processing. The reflectivity continued to fall at 50G, reaching 22.3%, and decreased further at 80G, registering at 19.2%, as the RAM process intensifies. However, there was an increase in reflectivity to 25.8% at 100G. This sequence of results from Figure 5-4 was crucial for understanding how RAM processing influences the surface properties of host powders, affecting their interaction with laser beam, particularly relevant for PBF-LB/M.

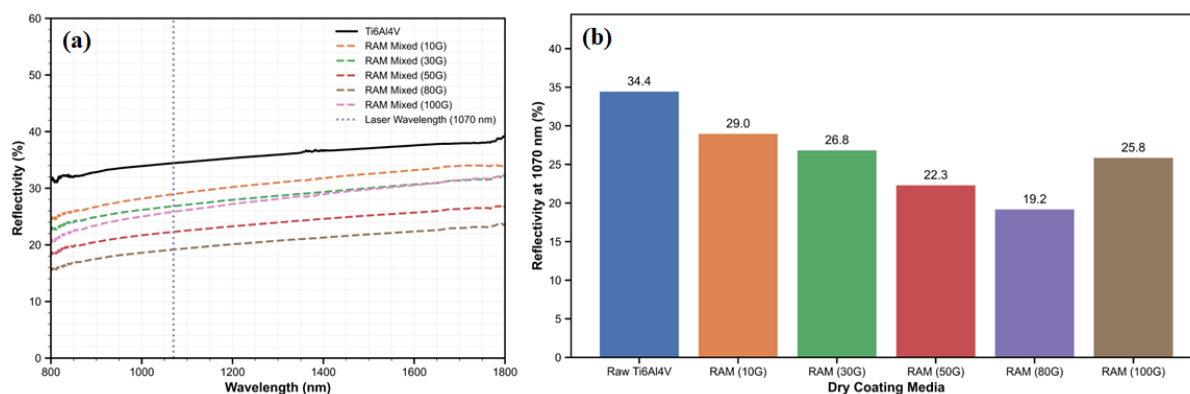


Figure 5-10 Reflectivity values of (a) Ti6Al4V and 0.1 wt.%B nanoparticle-decorated Ti6Al4V powders under 10-minute RAM processes at different gravitational accelerations; (b) Comparison of the reflectivity at the laser wavelength of 1070nm for Ti6Al4V and Ti6Al4V-0.1B composite powder. The dotted vertical line in (a) denotes the laser wavelength at 1070nm.

5.3.5 Assessment of Oxide Layer Thickness

The XPS survey spectra are insufficient for precisely discerning the intensity variations between the elemental peaks from the as-received surfaces to the target etching depths. Consequently, depth profiling via narrow scans over the specific binding energies of interest was employed to assess the elemental state transitions from oxides to metals. Figure 5-11 demonstrates this approach with detailed XPS depth profile spectra of the Ti2p, Al2p, V2p and O1s peaks, revealing the change in the composition of each element across different Ar⁺ etching depths. The Ti2p spectra (Figure 5-11(a)) showed a distinct shift in the Ti2p_{3/2} and Ti2p_{1/2} peak intensities as the etching depth increased, with the Ti2p_{3/2} peak initially at higher binding energies indicative of titanium oxide, gradually moving towards lower binding energies associated with metallic titanium. At shallower etching depths (9.0nm and 19.5nm), the presence of TiO₂ was pronounced as evidenced by the characteristic TiO₂ 2p_{3/2} peak at ~458.60eV, but as the etching progressed to depths of 40.5nm and beyond, the oxide peaks almost diminished and the metallic titanium peaks became more prominent, especially noticeable at the depth of 343.8nm where the Ti2p peaks closely resembled those of pure metallic titanium at ~453.79eV. This evolution of the spectra with etching depth quantitatively illustrated the reduction of titanium oxide layers, uncovering the underlying metallic titanium substrate. Additionally, Al2p spectra (Figure 5-11(b)) showed that Al2p³⁺ was initially indicated by a pronounced peak at ~74.30eV. As the etching depth increased, this oxide peak

attenuated, revealing a shift toward a lower binding energy indicative of metallic aluminum, which was centered $\sim 72\text{eV}$. In the V2p region (Figure 5-11(c)), the initial XPS spectra did not show any distinct peaks for vanadium metal or oxide, indicating that these species were not present or detectable on the surface layer. However, as the Ar^+ etching depth increased, V2p_{3/2} peak began to emerge around 512.4eV, corresponding to metallic vanadium. The XPS depth profile for the O1s region (Figure 5-11(d)) indicated changes in the oxygen content with increasing Ar^+ etching depths. Initially, the O1s spectra exhibited a high intensity, consistent with a significant presence of oxygen, likely in the form of surface oxides or adsorbed oxygen species. As the etching depth advanced, the intensity of the O1s peak decreased, reflecting a consistent reduction in oxygen content. This trend continued with deeper etching, suggesting the progressive removal of oxide layers, and revealing less oxidized material beneath the surface.

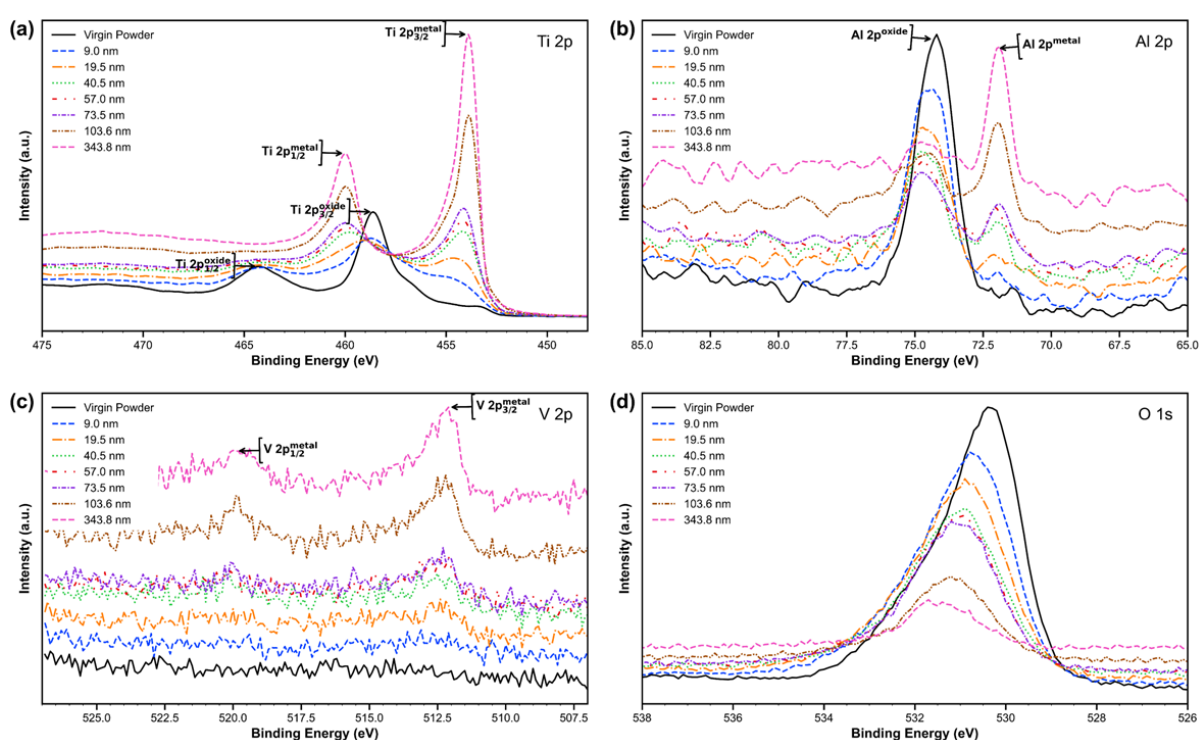


Figure 5-11 Detailed XPS depth profile spectra of (a) Ti 2p; (b) Al 2p; (c) V 2p and (d) O 1s peak composition change across Ar^+ etching depths.

The empirical data illustrated in Figure 5-12 encapsulates the effect of RAM process on the oxide layer thickness of Ti6Al4V alloy and boron-decorated Ti6Al4V composite powders. The oxide layer thickness on the pristine Ti6Al4V powder established a baseline at 104nm, as shown in Figure 5-12(a). When 0.1 wt% boron-decorated Ti6Al4V composite powder was subjected to a 10-minute RAM process at various acceleration gravities, notable variations in the oxide layer thickness were observed. At an acceleration gravity of 10G, the oxide layer reached a thickness of 100nm, depicted in Figure 5-12(b). Increasing the acceleration gravity to 30G resulted in a layer thickness of 95nm, as displayed in Figure 5-12(c). Further increments in the

acceleration gravity continued to influence the thickness. At 50G, the oxide layer thickness slightly reduced to 90nm, shown in Figure 5-12(d). The trend proceeded with the application of 80G, where the oxide layer registered a thickness of 82nm, as indicated in Figure 5-12(e). The maximum acceleration gravity tested, 100G, led to the thinnest oxide layer among the samples, measuring 78nm in thickness, as represented in Figure 5-12(f). These results, characterized by a decrease in oxide layer thickness with increasing acceleration gravity, delineate a clear trajectory of the impact of RAM processing parameters on the surface characteristics of boron-decorated composite powders. The progressive thinning of the oxide layer as the acceleration gravity is increased suggests a relationship between the mechanical forces applied during RAM and the structural responses of the powder surface. 100G condition markedly demonstrates the most considerable influence on the oxide layer thickness of composite powder.

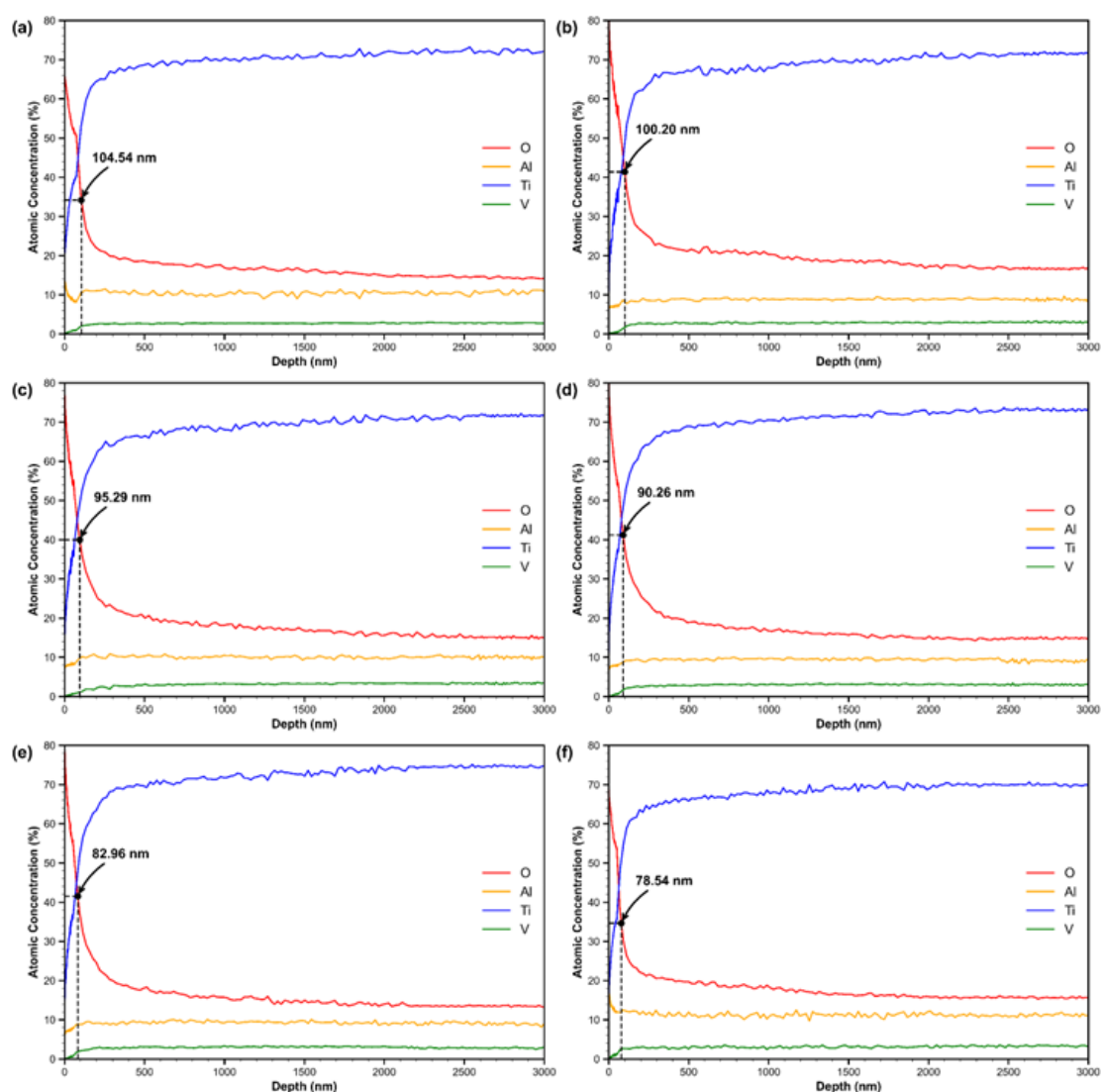


Figure 5-12 The atomic concentration of the surface as a function of etch depth for (a) Ti6Al4V powder; and 0.1 wt.%B modified Ti6Al4V powder under 10-minute RAM Mixing process at the acceleration gravity of (b) 10G; (c) 30G; (d) 50G; (e) 80G and (f) 100G.

5.4 Boron Nanoparticles Decoration of Ti6Al4V for PBF-LB/M

5.4.1 Phase Identification of Feedstock Powders

Figure 5-13 presents the XRD patterns of as-received Ti6Al4V and powders decorated with amorphous and crystalline boron via RAM technique. All specimens exhibit characteristic reflections of martensitic α' -titanium and TiO₂ with no additional crystalline phases detected, indicating that boron incorporation does not alter the fundamental phase constitution of the alloy (Chaithanya Kumar et al., 2024). The α' -titanium peaks were retained across all samples, while the 2θ peaks of TiO₂ near 25° and 64° confirmed the persistence of the native oxide layer (Guleryuz & Cimenoglu, 2009). When amorphous or crystalline boron is added to the alloy, the resulting XRD pattern showed the α' -titanium and TiO₂ peaks are retained, suggesting the incorporation of amorphous or crystalline boron does not introduce new phases but may cause slight variations in peak intensities. This implies that the structural integrity of the original phases is maintained with the addition of boron nanoparticles independent of its crystallinity. It is important to note that the XRD analysis did not detect boron on the surface of the composite powders. This limitation is due to the inherent constraints of XRD in detecting light elements like boron, particularly when they are present in small quantities or dispersed within the matrix (Epp, 2016; Shard, 2014). Notably, the boron-decorated powders exhibited a discernible broadening of α' -titanium peaks, signalling increased microstrain and reduced coherent domain size induced by high-energy milling during RAM (Fouzia et al., 2021; S. A. Kumar et al., 2014). These observations align with previous reports that mechanical attrition treatments refine crystallite dimensions and introduce lattice strain without generating new phases (Bilous et al., 2005; Guleryuz & Cimenoglu, 2009; S. Yuan et al., 2022). Overall, the addition of both amorphous and crystalline boron to Ti6Al4V did not alter the primary phase composition of the alloy, as all modified samples continue to exhibit the α' -titanium and TiO₂ phases. Previous studies have demonstrated that RAM process leads to increased microstrain and smaller crystalline sizes, which is consistent with the observed XRD patterns.

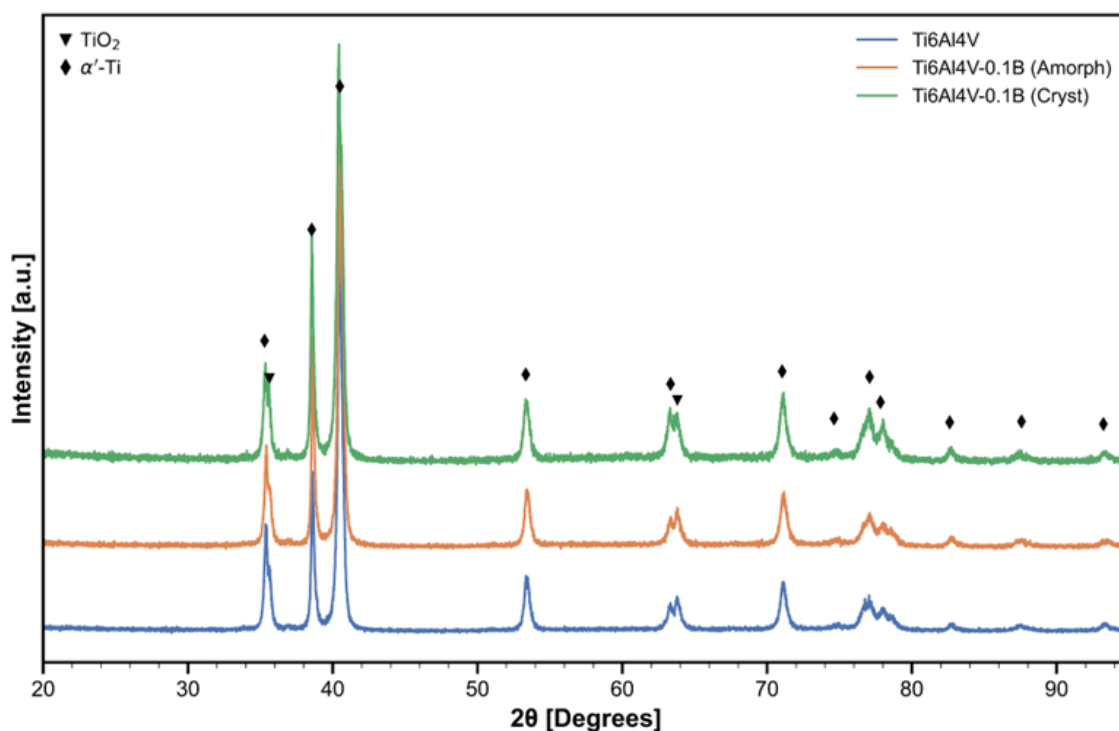


Figure 5-13 Comparative X-ray diffraction patterns of raw and 0.1 wt.%B nanoparticle-decorated Ti6Al4V powders under 10-minute RAM process at 50G-force.

Figure 5-14 presents the wide-scan XPS survey spectra of unmodified Ti6Al4V alongside powders decorated with amorphous and crystalline boron via RAM processing. In the spectrum of the untreated alloy, only the characteristic Ti2p, Al2p, O1s and C1s peaks are observed, with no detectable B1s signal. By contrast, both boron-decorated samples exhibit an additional high-energy feature at binding energy of approximately 190 eV, corresponding to the B1s core level, which definitively confirms surface incorporation of boron (Peretti et al., 2018; Türkmen et al., 2022; Wagner, 1991). High-resolution inspection of the Ti2p region reveals two spin-orbit components at binding energy of around 458.5 eV (Ti2p_{3/2}) and around 464.2 eV (Ti2p_{1/2}), which remain essentially unchanged after boron decoration (Hierro-Oliva et al., 2014). This invariance demonstrates that both the metallic and oxidised states of titanium within the Ti6Al4V matrix are preserved following surface treatment, indicating minimal disturbance to the underlying substrate chemistry (Durdu et al., 2013; Wagner, 1991). Similarly, the Al2p, O1s and C1s core-level peaks—located at binding energies approximately 74.6eV, 532.1eV and 284.8eV, respectively—exhibit no measurable shifts in binding energy or peak intensity upon boron incorporation. This consistency confirms that the native alumina film, oxygen-containing species and adventitious carbon layer on Ti6Al4V remain intact throughout the RAM decoration process, preserving the primary surface composition (do Nascimento et al., 2021; Hierro-Oliva et al., 2014; Wagner, 1991).

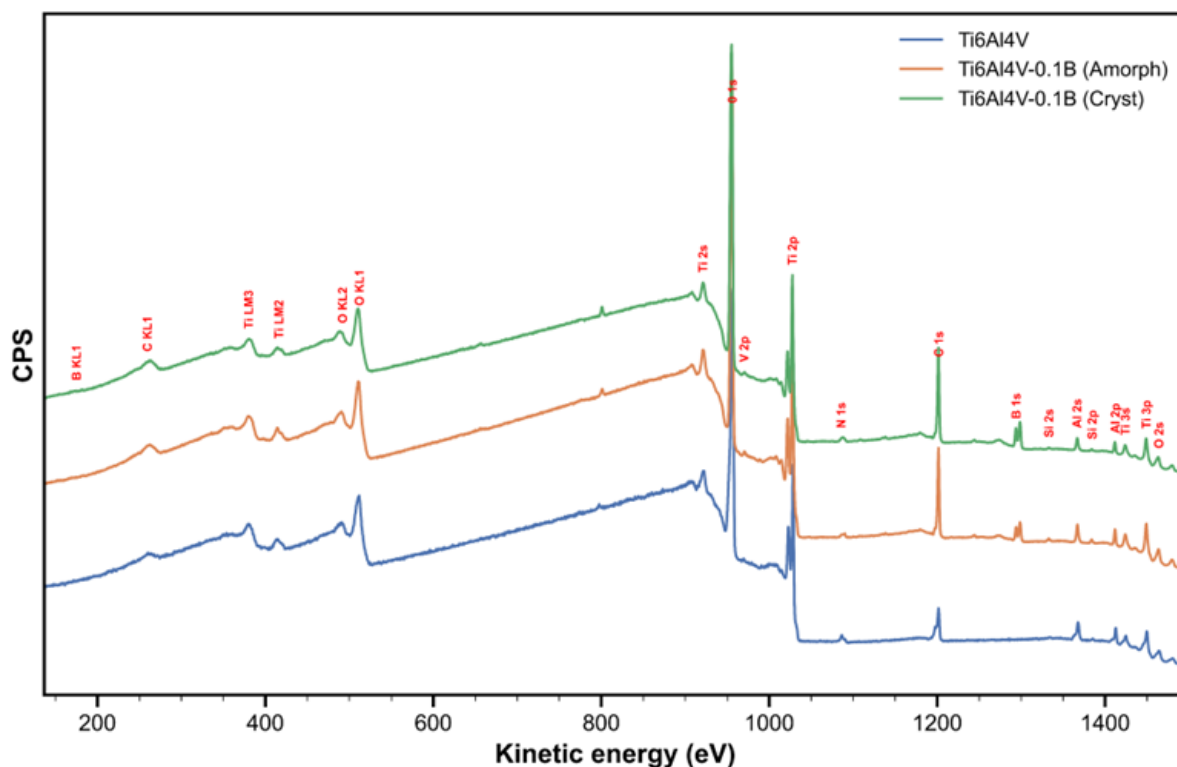


Figure 5-14 XPS Survey spectra of raw and 0.1 wt.%B nanoparticle-decorated Ti6Al4V powders under 10-minute RAM process at 50G-force.

5.4.2 Powder Morphology of Feedstock Powders

Figure 5-15 presents SEM (SE) micrographs comparing the surface morphology of raw and 0.1 wt.% B-modified Ti6Al4V powders after a 10-minute RAM process at 50G-force. In Figure 5-15(a), the raw powder exhibited a smooth and uniform surface, indicative of its pristine state. Figure 5-15(b) shows the Ti6Al4V powder modified with amorphous boron nanoparticles, where the surface appears slightly roughened and coated, suggesting successful adhesion of the nanoparticles. Figure 5-15(c) depicts the Ti6Al4V powder modified with crystalline boron nanoparticles, revealing a more textured surface compared to the amorphous counterpart, yet successful adhesion of nanoparticles was still present. High magnification images in Figure 5-15(d) and (e) offered detailed insights into the surface characteristics of the modified powders. Figure 5-15(d) focuses on the amorphous boron-modified powder, where small, evenly distributed boron nanoparticles can be seen adhering to the Ti6Al4V surface. This indicates a uniform coating and integration of boron nanoparticles into the powder matrix. Figure 5-15(e) shows the crystalline boron-modified powder, displaying a rougher and more irregular surface, with larger boron particles creating a more pronounced texture. The distinct shape and size of crystalline particles was thought to contribute to a more uneven surface morphology. These micrographs collectively illustrate that the RAM process at 50G-force effectively integrated boron nanoparticles onto Ti6Al4V powder surfaces. The amorphous

boron provides a smoother, more uniform coating, whereas crystalline boron resulted in a rougher, more textured surface.

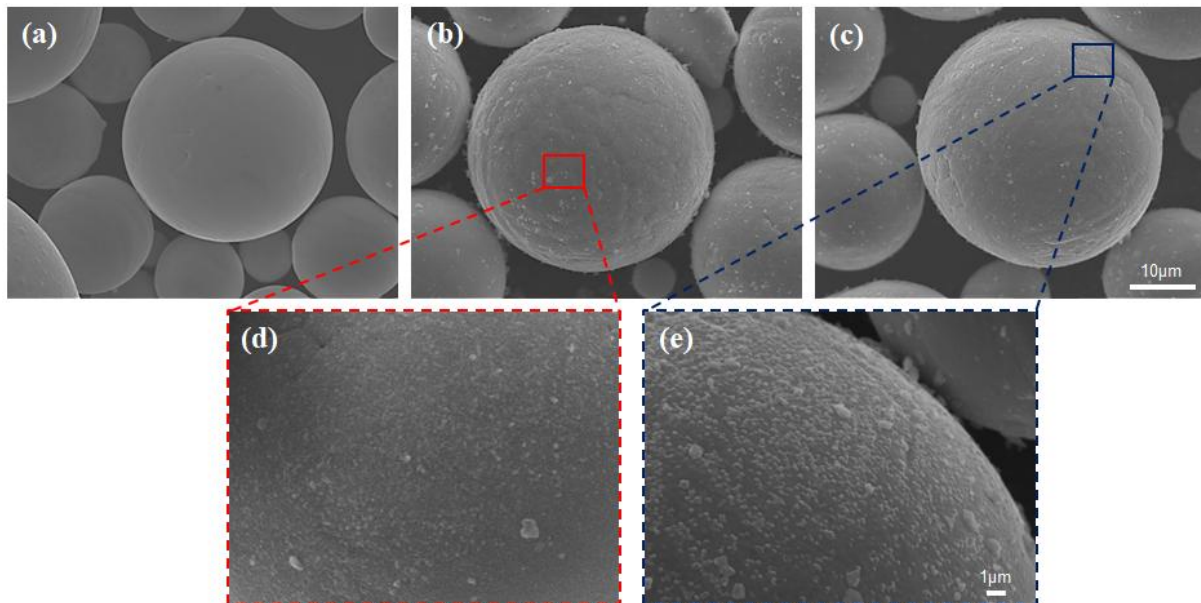


Figure 5-15 SEM (SE) micrographs of (a) raw Ti6Al4V; and 0.1 wt.%B-modified composite powders with (b) amorphous boron and (c) crystalline boron under 10-minute RAM process at 50G-force. High magnification images of composite powder surfaces for (d) amorphous boron-modified and (e) crystalline boron-modified powders.

Figure 5-16 presents SEM (SE) images and corresponding EDX elemental maps of titanium and boron for raw powder and 0.1 wt.% Boron-modified composite powders, subjected to a 10-minute RAM process at 50G-force. In Figure 5-16(a), the SEM image of raw powder revealed smooth and uniform particles. The EDX map for titanium showed a homogeneous distribution of titanium across the analysed particles, while elemental boron was not detected, as expected for the unmodified powder. Figure 5-16(b) shows the SEM image of Ti6Al4V powder mixed with amorphous boron nanoparticles. The surface of the particles appeared roughened with visible small particles adhering to the surface. The EDX map for titanium remained uniform, indicating consistent titanium distribution as expected. The EDX map for boron showed a scattered distribution of boron particles across the surfaces, confirming the successful incorporation of amorphous boron. Figure 5-16(c) depicts the SEM image of Ti6Al4V powder mixed with crystalline boron nanoparticles. The particles displayed a more textured surface compared to the amorphous variant. The EDX map for titanium was consistent with previous samples, showing uniform titanium presence. The EDX map for boron indicated a more widespread and uniform distribution of crystalline boron nanoparticles on the surface, highlighting the effective decoration achieved through the RAM process.

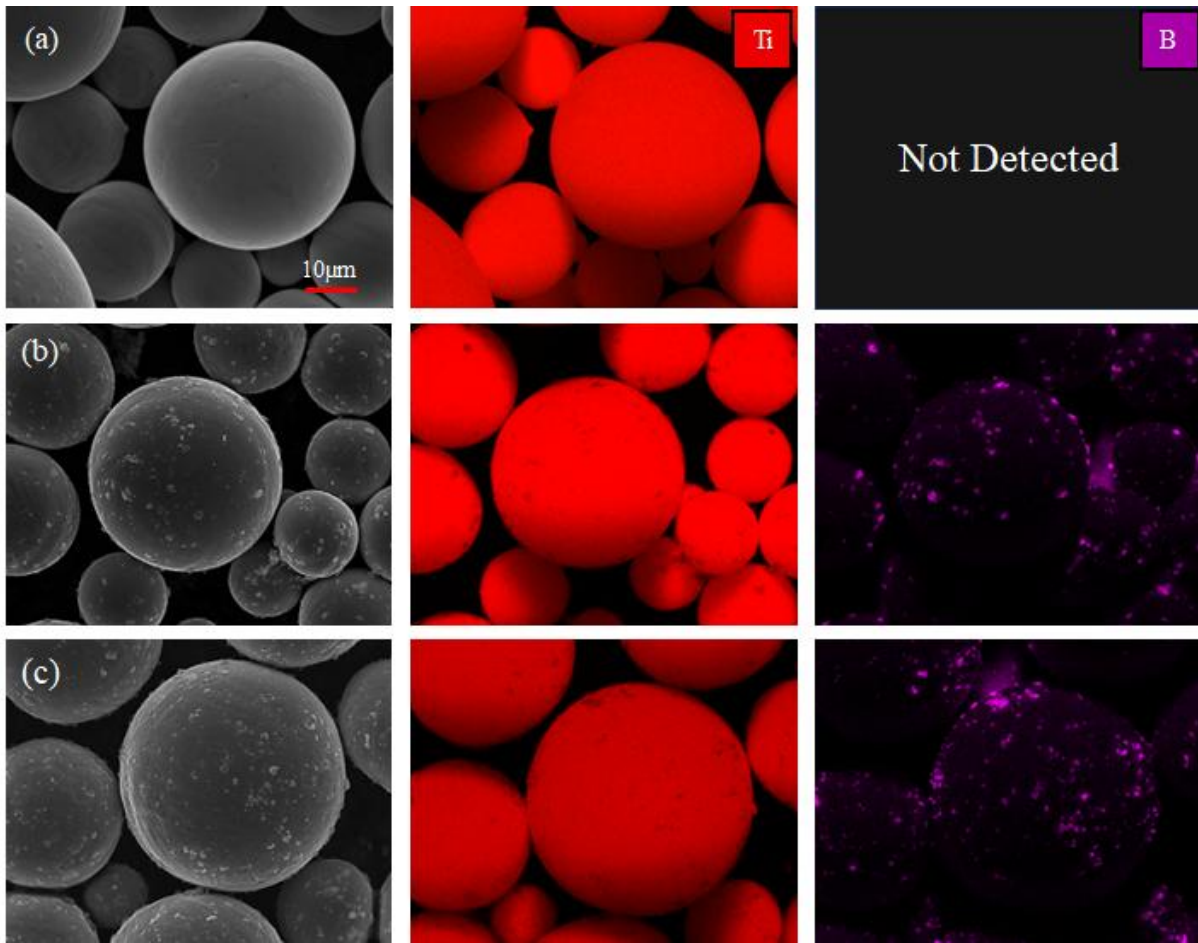


Figure 5-16 SEM (SE) images (left) of the powders and corresponding EDX elemental maps of Ti (middle) and B (right) for (a) raw Ti6Al4V; and 0.1 wt.%B-modified composite powders with (b) amorphous boron and (c) crystalline boron under 10-minute RAM process at 50G-force.

5.4.3 Flow Properties of Feedstock Powders

Table 5-4 summarises the dynamic flow properties of unmodified Ti6Al4V powder and powders decorated with 0.1 wt.%B nanoparticles at 50G gravitational acceleration. The Basic Flowability Energy (BFE)—defined as the energy required to displace a conditioned volume of powder under confinement—decreased from 13.861mJ for the raw powder to 12.103mJ after amorphous boron decoration and further to 11.848mJ with crystalline boron, indicating a progressive improvement in flowability (Freeman, 2007; Leturia et al., 2014). The stability index, which quantifies the variation in flow energy during successive consolidation and flow cycles, fell marginally from 0.985 in the untreated powder to 0.945 (amorphous) and 0.932 (crystalline) boron-decorated samples, reflecting a slight enhancement in resistance to compaction-induced fluctuations (Hare et al., 2015). The flow rate index—measuring the sensitivity of flow energy to blade velocity—remained essentially constant at 1.303 for the raw and amorphous-decorated powders, with only a minor rise to 1.318 for the crystalline form, suggesting that boron addition does not appreciably alter strain-rate dependency under these

conditions (Hare et al., 2015). Specific Energy (SE), the energy per unit mass required to initiate unconfined flow, decreased from 0.501mJ/g in the as-received powder to 0.413mJ/g for amorphous-boron modified powder and 0.381mJ/g for crystalline-boron modified powder, consistent with reduced interparticle cohesion and facilitated flow initiation (Dattani, n.d.; Freeman, 2007). Finally, the conditional bulk density exhibited a slight increase from 2.641 gcm⁻³ in the raw powder to 2.660 gcm⁻³ and 2.683 gcm⁻³ for the amorphous and crystalline boron-decorated powders respectively, indicating improved packing efficiency in nanoparticle-modified feeds (Dattani, n.d.; Y. Sun et al., 2018). Similar enhancements in bulk density have been reported for Ti6Al4V powders decorated with two-dimensional nanocarbon (M. Dong et al., 2022) and in situ TiC/Ti6Al4V composites (G. Shi et al., 2023). Taken together, these results demonstrate that surface decoration of Ti6Al4V powders with boron—particularly in crystalline form—substantially improves their dynamic flow characteristics and bulk density under high-gravity RAM processing, thereby enhancing their suitability for downstream additive manufacturing operations.

Table 5-4 Comparison of the dynamic flow properties of raw and 0.1 wt.%B nanoparticle-decorated Ti6Al4V powders processed prepared at 50G.

<i>Processing Method</i>	<i>BFE (mJ)</i>	<i>SI</i>	<i>FRI</i>	<i>SE (mJ/g)</i>	<i>CBD (g/cc)</i>
Raw Ti6Al4V	13.861	0.985	1.303	0.501	2.641
Ti6Al4V-0.1B (Amorph)	12.103	0.945	1.303	0.413	2.660
Ti6Al4V-0.1B (Cryst)	11.848	0.932	1.318	0.381	2.683

Figure 5-17 illustrates the flow functions of Ti6Al4V and its 0.1 wt.%B nanoparticle-decorated variants (both amorphous and crystalline) after a 10-minute RAM process at 50G. The graph depicts the unconfined yield strength (σ_c) against the consolidation stress (σ_1), highlighting the flowability characteristics of each powder type. The raw powder exhibited the highest unconfined yield strength across all consolidation stresses, indicating lower flowability compared to the boron-decorated powders. The composite powder decorated with amorphous boron nanoparticles demonstrated intermediate flow properties, with a noticeable reduction in unconfined yield strength compared to the raw powder, suggesting enhanced flowability due to amorphous boron decoration. The composite powder decorated by crystalline boron nanoparticles showed the lowest unconfined yield strength among the samples, reflecting the greatest improvement in flowability after mixing with crystalline boron. The dotted lines representing flow function coefficients show that All powders lie within the easy flow region for the applied consolidation stresses, with the crystalline Boron-decorated powder achieving the highest flow function coefficient. This data indicates that Boron nanoparticle decoration, particularly in the crystalline form, significantly enhances the flow properties of Ti6Al4V powders, making them more suitable for industrial applications requiring high flowability and reduced inter-particulate friction.

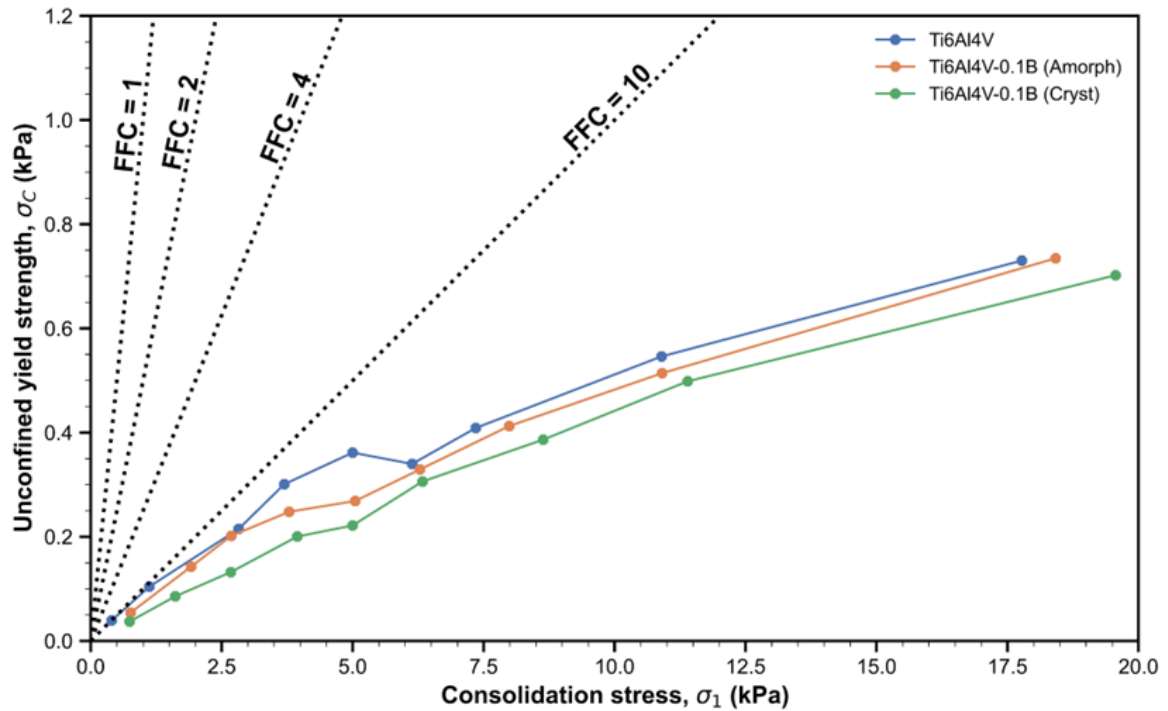


Figure 5-17 Flow functions of raw and 0.1 wt.%B nanoparticle-decorated Ti6Al4V powders subjected to 10-minute RAM processes at 50G-force.

Table 5-5 presents the average shear properties of raw and 0.1 wt.%B nanoparticle-decorated Ti6Al4V powders subjected to a 10-minute RAM process at 50G-force. Cohesion—defined as the unconfined yield strength extrapolated from the yield locus—decreased markedly from 0.122kPa in the as-received powder to 0.078kPa amorphous-boron decorated and 0.054kPa crystalline-boron decorated powder, demonstrating a significant reduction in interparticle adhesion owing to nanoscale boron disrupting van der Waals and electrostatic interactions (Y. Wang et al., 2016). This reduction in cohesion aligns with similar trends observed in other nanoparticle-modified powders (Ghadiri et al., 2020). The angle of internal friction (AIF)—the gradient of the Mohr yield locus—fell from 14.469° in the raw powder to 13.599° and 12.723° for amorphous and crystalline boron-decorated samples respectively, indicative of easier particle sliding facilitated by surface-adsorbed boron (Anton Paar GmbH, n.d.). Concurrently, the flow function coefficient (FFC)—the ratio of major principal consolidation stress to unconfined yield strength—increased from 16.89 for as-received powder to 24.99 amorphous-boron modified powder and 25.54 crystalline-boron modified powder, effecting a transition from ‘cohesive’ to ‘free-flowing’ powder behaviour in accordance with Jenike’s classification (Jenike, 1976; Mariano, 2024; Y. Wang et al., 2016). Similar enhancements in shear performance have been documented for Ti6Al4V powders decorated with two-dimensional nanocarbon, where cohesion dropped and FFC rose correspondingly (M. Dong et al., 2022), and for in situ TiC/Ti6Al4V composites, which exhibited enhanced flowability and reduced shear stress requirements (G. Shi et al., 2023). Collectively, these results confirm that boron nanoparticle decoration—particularly in its crystalline form—effectively optimises the shear

properties of Ti6Al4V powders, promoting improved powder-bed spreading, reduced recoater forces and enhanced build uniformity in additive manufacturing (ASTM International 2002).

Table 5-5 Average shear properties of raw and 0.1 wt.%B nanoparticle-decorated Ti6Al4V powders under 10-minute RAM processes at 50G-force.

<i>Processing Method</i>	<i>Cohesion (kPa)</i>	<i>AIF (°)</i>	<i>FFC</i>
Raw Ti6Al4V	0.122 ± 0.080	16.469 ± 1.726	16.89 ± 6.06
Ti6Al4V-0.1B (Amorph)	0.078 ± 0.032	13.599 ± 1.171	24.99 ± 5.74
Ti6Al4V-0.1B (Cryst)	0.054 ± 0.053	12.723 ± 1.085	25.54 ± 3.22

5.4.4 Laser Reflectivity Measurements

Figure 5-18 presents the diffuse reflectance spectra of as-received Ti6Al4V powder and powders decorated with 0.1 wt.% amorphous and crystalline boron nanoparticles. The as-received powder exhibited a high, nearly flat reflectivity of approximately 32–38% across 800 – 1800nm, consistent with prior characterisations of gas-atomised Ti6Al4V powder (D. He et al., 2023; D. Zhang, Wang, et al., 2019) and corroborated by in-situ monitoring studies reporting similar reflectance values upon oxidation (Soundarapandiyar et al., 2023). Decoration with amorphous boron nanoparticles induced an overall downward shift of the reflectance curve by ~12%, reflecting both the intrinsic ~22% near-IR reflectance of amorphous boron films (Kuhlmann et al., 1994) and increased surface roughness that promotes multiple scattering events (Hou et al., 2023). The sample decorated with crystalline boron displays the most pronounced suppression, with reflectance decreasing by an additional ~3% relative to the amorphous case, in line with the inherently lower ~15–20% reflectance of β -rhombohedral boron at 1 μ m (Werheit, 1988). Figure 5-18(b) quantifies these differences at the PBF-LB/M laser wavelength of 1070nm, where reflectivity falls from 34.4% for as-received powder to 22.3% for amorphous-boron modified powder and 19.3% crystalline-boron modified powder (Alsaddah et al., 2021; Cook & Ritchie, 2023). These measurements imply a corresponding increase in laser absorptivity from ~65% to ~78% and ~81%, respectively, thereby substantially enhancing energy coupling in the powder bed. Numerical simulations further indicate that such reductions in powder reflectivity can improve melt-pool stability and reduce keyholing instabilities by up to 25% under typical PBF-LB/M conditions (D. Zhang, Wang, et al., 2019). Mechanistically, the dual effect of low intrinsic reflectance and the nanoscale roughening of boron nanoparticles introduced during RAM decoration leads to enhanced light trapping via Fresnel-angle scattering and sub-wavelength surface plasmon effects (L. Zhou et al., 2024). Similar strategies—such as LaB₆ or 2D nano-carbon additives—have demonstrated comparable reflectance suppression and absorptivity gains in Ti6Al4V powders (M. Dong et al., 2022; D. He et al., 2023). By lowering the powder-bed reflectance from ~34% to ~19% at 1070nm, crystalline boron decoration offers a viable route to reduce laser power requirements, minimise spatter generation and enhance part density in PBF-LB/M processes (Gruber et al., 2025; Soltani-Tehrani et al., 2022).

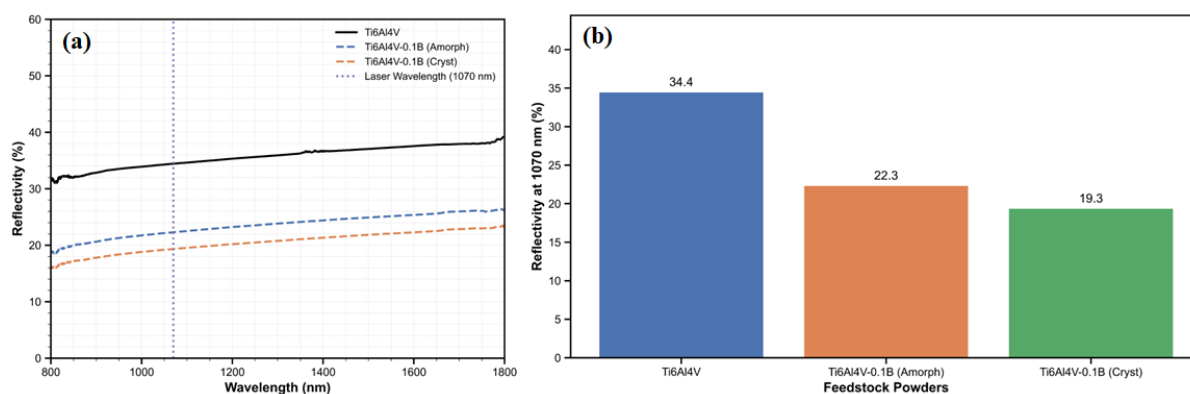


Figure 5-18 Reflectivity values of (a) Ti6Al4V and 0.1 wt.%B nanoparticle-decorated Ti6Al4V powders under 10-minute RAM processes at 50G-force; (b) Comparison of the reflectivity at the laser wavelength of 1070nm for Ti6Al4V and Ti6Al4V-0.1B composite powder. The dotted vertical line in (a) denotes the laser wavelength at 1070nm.

5.5 Discussion

5.5.1 Effect of Gravitational Acceleration on Mixing Performance

XRD patterns demonstrated the presence of the α' -titanium phase and a notable reduction in TiO_2 content from approximately 7% in the host powder to about 3% post-RAM processing, with respect to the applied gravitational force. This reduction in TiO_2 indicates the efficacy of the RAM process in altering the oxide phase composition. The RAM process effectively reduces the TiO_2 content by introducing mechanical energy that likely facilitates the breaking down and redistribution of oxide phases within the powder matrix. Furthermore, the increase in microstrain and decrease in crystallite size are attributed to the mechanical stresses and lattice distortions induced by the RAM process. The progressive broadening of diffraction peaks with increasing gravitational force indicates more significant lattice distortions and plastic deformation. The slight increase in crystallite size at the highest force suggests a balance between grain refinement and re-agglomeration or other mechanisms that limit further size reduction. The incorporation of guest nanoparticles onto the host surface at higher RAM intensities results from increased mechanical energy facilitating better dispersion and adherence of nanoparticles. However, at very high forces, the kinetic energy might exceed adhesive forces, causing a 'bouncing' effect where guest particles are less likely to adhere. This phenomenon highlights the importance of optimizing gravitational forces to achieve effective surface modification.

To further understand the impact of material properties and processing conditions on coating performance, it is essential to consider the stiffness of guest particles and the stick/bounce model. Stiffness, represented by Young's modulus, of guest particles affects coating performance, even under identical processing conditions Boron stiffness varies with crystalline form and purity. Literature estimates amorphous boron stiffness at 320 – 380GPa, but it can differ from bulk value due to the surface effects, and potential changes in crystal structure at

the nanoscale(L. Cao et al., 2002; L. Guo et al., 2006). Due to inverse Hall-Petch correlation with size of guest particles, it is assumed nanoparticles will be more ductile compared to bulk metal(Casati & Vedani, 2014). The stick/bounce model was used to evaluate quality indices for coating (K_c) and de-agglomeration (K_d). Figure 5-19(a) shows the quality indices for K_c and K_d as a function of gravitational accelerations. K_c decreases with increasing intensity using either guest material, indicating that guest particles tend to bounce off at high gravitational accelerations. In addition, $K_c \geq 1$ occurs for the intensities below 4G and 12G for rigid and ductile guest particles, respectively. This indicates good coating performances would be reached when using processing intensities below these values, for the respective guest materials, although it is possible that such low intensities may not provide adequate mixing action between the host and guest materials. The coating performances observed in Figure 5-19(b) and (c) are in line with model estimation. When host particle decorated with ductile nanoparticles that is agglomerated, the best coating performance was attained when processed at 5G. However, host particles were not well coated at higher intensities like 100G due to bouncing off effect. Furthermore, to assess guest particle agglomeration tendency, K_d was computed and found to be less than 1 (indicating adequate deagglomeration of guest particles) above 2G and 6G for rigid and ductile guest particles, respectively.

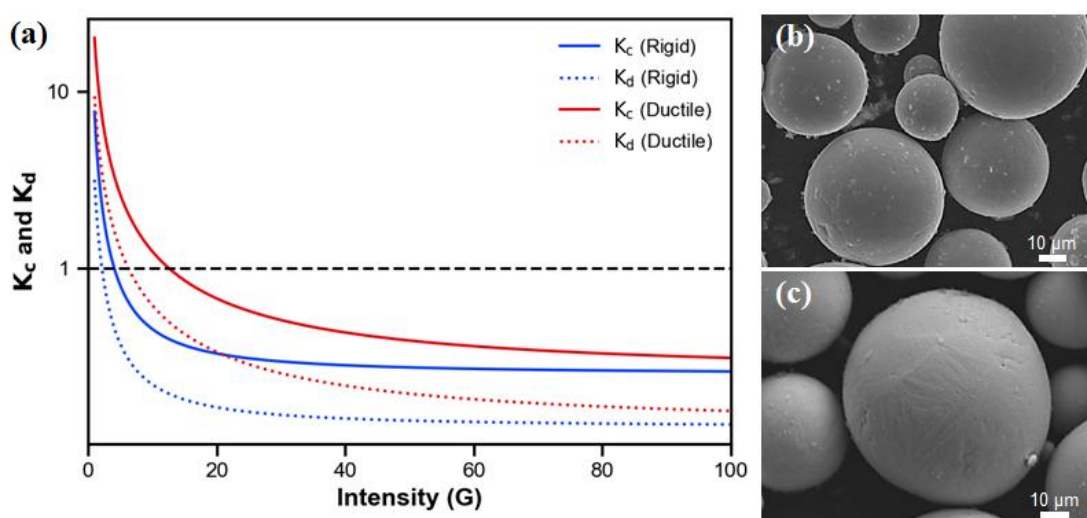


Figure 5-19 (a) Quality indices for dry coating (K_c) and de-agglomeration (K_d) for the coating assessment of Ti6Al4V decorated with agglomerated nanoparticles having different stiffnesses; and 10-minute mixing at (b) 5G and (c) 100G.

The model was also used to evaluate guest particle stiffness on coating performance. In Figure 5-20, guest and host particle radii are fixed at 1 μm and 32 μm , mimicking agglomerated nanoparticles and host particle. Figure 5-20 illustrates the total detachment energy decreases with increasing stiffness, indicating harder guest particles have an increasing tendency to bounce off host particles. The relative kinetic energy remains constant, being independent of stiffness. When the stiffness is about 340GPa, total detachment energy equals to relative kinetic energy, suggesting that for optimal coating quality, guest particles should have stiffness below

this threshold when processed at 50G. As stiffness increases, both van-der-Waals energy and deagglomeration energy decrease due to smaller indentation depths and contact areas. In other words, more ductile guest particles create larger indentation depths and require more energy for separation. Generally, harder guest particles need less energy to bounce off, indicating that lower stiffness is preferable for better coating performance, except when the host particle is very soft. Conversely, higher guest particle stiffness is favourable for deagglomeration. Notably, plastic deformation energy remains relatively constant because increased stiffness enhances collision force but reduces collision time and indentation depth simultaneously, resulting in relatively net zero change in plastic deformation energy.

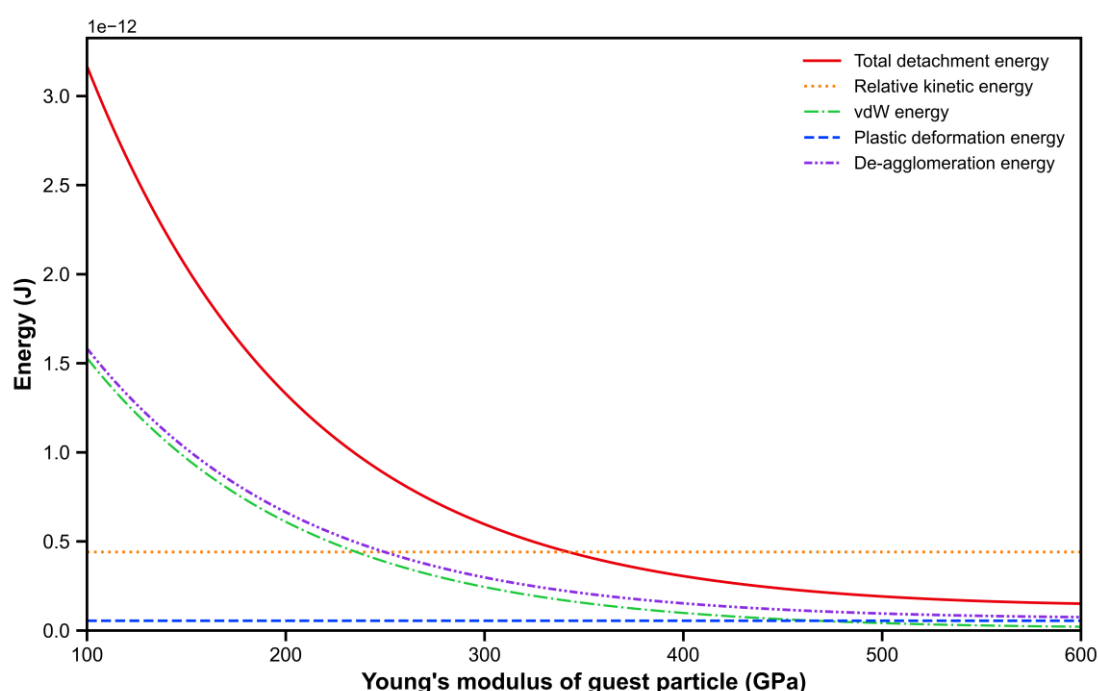


Figure 5-20 Effect of guest particle stiffness on interparticle energies at gravitational acceleration of 50G.

In addition to stiffness, guest particle size significantly influences dry particle coating. Smaller particles enhance surface adhesion due to their higher surface area-to-volume ratio but may agglomerate due to van-der-Waals forces. Larger particles may not adhere as effectively, leading to uneven coatings. Optimal performance balances particle size to maximize adhesion while minimizing agglomeration and bounce-off effects. This size effect may also be explained using the stick/bounce model. K_c and K_d quality estimations were calculated and plotted in Figure 5-21 as a function of gravitational accelerations. When $K_c \geq 1$, nano-sized guest particles tend to stick to host surfaces across all gravitational accelerations. Conversely, agglomerated guest particles tend to bounce off the host surface when $K_c < 1$. Figure 5-21(b) and (c) illustrate the coating performance as a function of particle size after 10-minute mixing at 50G. In terms of guest agglomeration, K_d decreased with increasing mixing intensity in both cases, indicating improved deagglomeration with increasing mixing intensity. However, even at very high

gravitational accelerations, K_d remains much larger than 1 for nano-sized particles, indicating presence of guest particle agglomeration at these intensities, as shown in Figure 5-21(c).

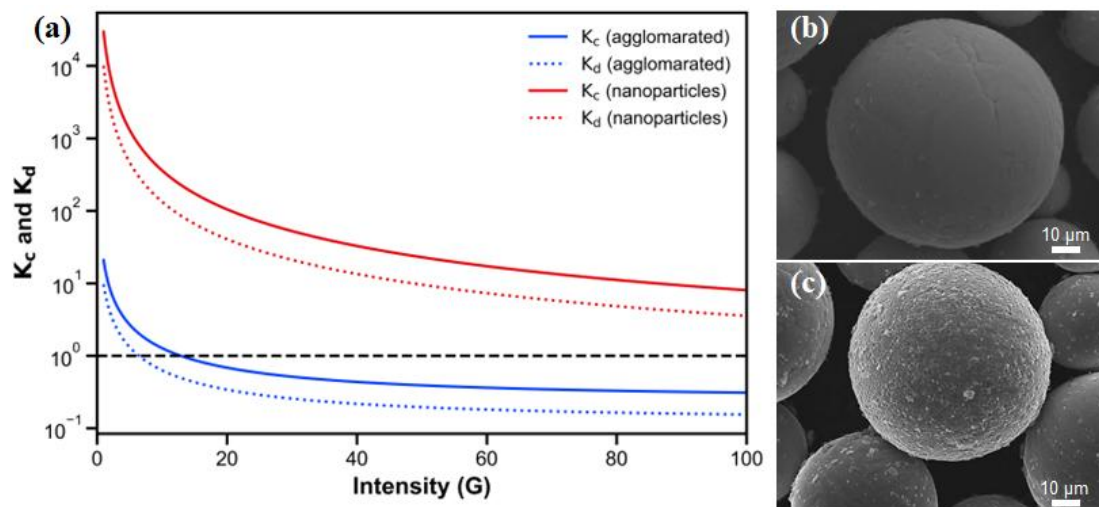


Figure 5-21 (a) Quality indices (K_c and K_d) for Ti6Al4V with micron and nano-sized guest particles; (b) micron-sized coating and (c) nano-sized coating after 10-minute mixing at 50G.

The model for the fixed size of host particles (32 μm) and mixing intensity of 50G was used to assess the impact of guest particle size on interparticle energies (see Figure 5-22). The results indicate when guest particle size increases, the total detachment energy exceeds the relative kinetic energy if the guest particle size is below 0.2 μm , suggesting guest particles smaller than 0.2 μm adhere to host particles. Conversely, guest particles larger than 0.3 μm are likely to bounce off. As the guest particle size increases, the relative kinetic energy increases more rapidly than the other energies, highlighting its sensitivity to guest particle size. Moreover, relative kinetic energy is lower than the de-agglomeration energy for guest particles below 0.1 μm , indicating a tendency for these particles to form agglomerates. In addition, total detachment energy, as well as all other energies increase with increasing guest particle size. Larger guest particles result in higher collision forces, leading to greater deformation/contact areas of the particles. Greater deformation corresponds to higher van-der-Waals and plastic deformation energy. An interesting observation is that for smaller guest particles ($\leq \sim 0.5\mu\text{m}$), the total detachment energy is dominated by van-der-Waals energy, whereas for larger guest particles ($\geq 0.5\mu\text{m}$), it is dominated by de-agglomeration energy. This shows the de-agglomeration step consumes the most energy when guest particles are 0.5 μm or larger (Deng et al., 2018; Nguyen et al., 2015). In summary, nano and sub-micron sized guest particles tend to agglomerate, while larger micro-sized guest particles lead to the separation of host and guest particles during the dry powder coating process. Thus, using higher processing intensities and/or larger guest particle sizes may result in poor dry powder coating.

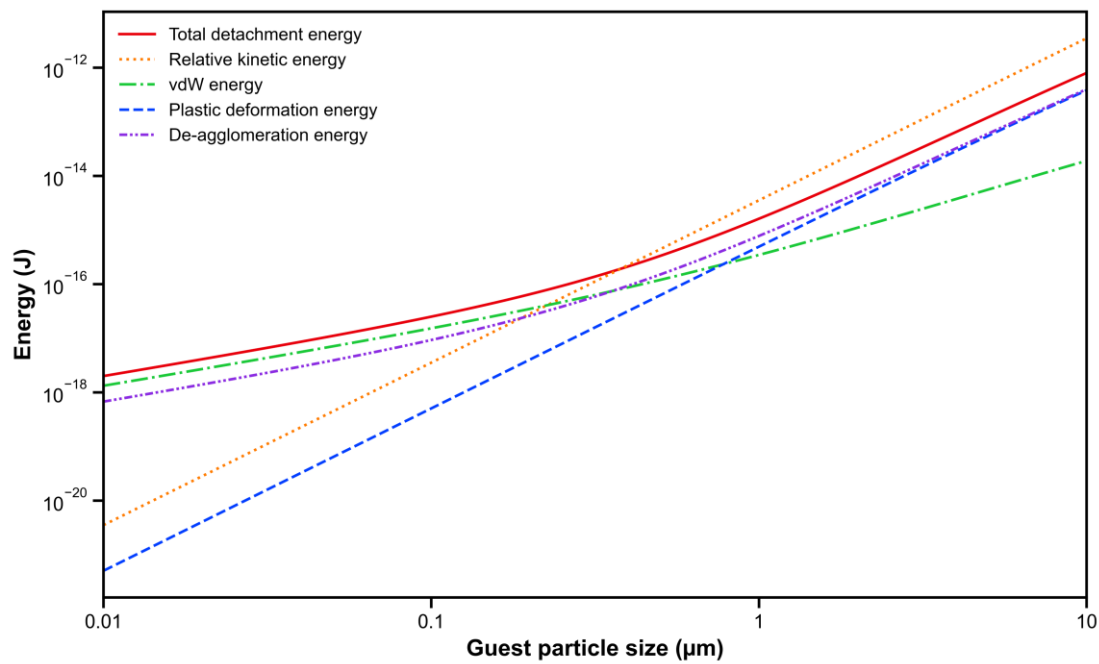


Figure 5-22 Effect of guest particle size on interparticle energies at gravitational acceleration of 50G.

5.5.2 Influence of RAM Conditions on Reflectivity

The introduction of various RAM mixing parameters had a clear influence on the reflectivity behaviour of the raw powder. The change in the reflectivity values was not due to a change in particle size, as the PSD results were consistent. Instead, the introduction of nanoparticle-decoration was a determinant factor. A uniform layer of nanopowder, with its tiny grain size, may present a rough and consistent surface interface altering the interaction between incident light and the substrate (Karg et al., 2019; Lüddecke et al., 2021). The increase in absorptivity with increasing applied gravitational accelerations can be attributed to a phenomenon observed in laser interactions with rough surfaces, where the inherent surface roughness and treatment-induced topographical changes cause multiple reflections and potential beam absorption (Y. Li et al., 2021; Mattern et al., 2019). At very low angles of incidence, the reflected beam can be directed deeper into the powder bed (Figure 5-23(a) – 2), introducing multiple reflections and potentially complete absorption by the powder bed (Y. Li et al., 2021). These are known as partial beam traps. A similar effect occurs when a beam directly hits a gap between two top layer powders (Figure 5-23(a) – 1). Conversely, as illustrated by beam 3 in Figure 5-23(a), a beam can be reflected away from the powder bed through a simple reflection, resulting in scattering losses that do not impact the process. Overall, multiple reflections significantly enhance absorbance by increasing the occurrences of absorption (Y. Yang et al., 2018). The surface decoration introduces an additional dynamic influencing the absorption properties of the powder particles. Multiple reflections can occur at the interfaces between the atmosphere, the decorated layer, and the metal substrate at specific angles of incidence. Depending on the wavelength and the chemical composition of the surface decoration, a greater percentage of radiation may be absorbed or reflected compared to the base material (Querry et al., 1985).

Moreover, unique oxides within the surface decoration can create a refractive index gradient, enhancing the amount of light coupled into the material (Suomela et al., 2013). Interference effects may also arise within dielectric layers of the decoration, leading to variations in absorption at certain layer thicknesses and wavelengths (Koushki et al., 2015).

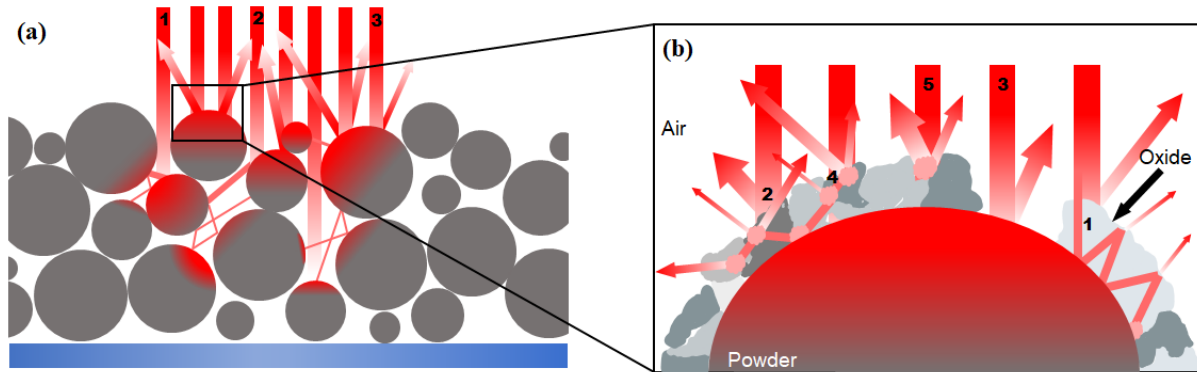


Figure 5-23 Schematic of (a) laser absorption on powder surfaces and (b) magnified view of a powder particle with nanoparticle and oxide accumulation on the surface.

In PBF-LB/M and other laser-based manufacturing processes, the role of surface oxides on metal powders is crucial due to their significant impact on laser-material interactions. These surface oxides can take various forms, such as amorphous layers, polycrystalline conglomerates, or oxide whiskers (Bauer et al., 2017). The presence of surface oxide introduces an additional factor influencing the absorption of laser energy by the powder particles. Multiple reflections can occur between the interfaces of the atmosphere, the oxide layer, and the metal at specific angles of incidence (Figure 5-23(b) – 1). Depending on the wavelength and chemical composition of oxides, a greater portion of radiation can either be absorbed or reflected (Figure 5-23(b) – 2), in contrast to the base material (Figure 5-23(b) – 3) (Querry et al., 1985). Additionally, unique oxide formations can create a refractive index gradient, enhancing the amount of light entering the material (Suomela et al., 2013), and interference effects may arise in dielectric oxide layers, altering absorption at certain layer thicknesses and wavelengths (Koushki et al., 2015). Conversely, polycrystalline oxide conglomerates or layers increase light scattering due to refractive index differences at grain boundaries (Figure 5-23(b) – 4) (Apetz & Van Bruggen, 2003). Amorphous mixed oxide layers, which also vary in refractive indices, contribute to scattering effects and may contain pores that further scatter light (Figure 5-23(b) – 5). This scattering is exacerbated by the powder surface where multiple reflections among individual oxidized particles increase scattering in the upper layers, preventing laser radiation from penetrating deeper into the powder bed. Similarly, polycrystalline alumina used in diffuse reflectors, enhances this effect by increasing the reflectance of the powder, thereby reducing absorbance (Apetz & Van Bruggen, 2003).

5.5.3 Influence of RAM Conditions on Flowability

The dynamic flow properties of alloy powders were significantly influenced by the application of RAM at varying gravitational accelerations. Since Boron-decorated host particles retains the same spherical morphology as raw host particles, powder morphology cannot be predominant in the flowability variations in RAM processed powders. Accordingly, the change in flow properties can mainly be attributed to the guest-decorated host particles, as schematically illustrated in Figure 5-24. The guest decoration may cause two different interactions affecting flow characteristic. While the mechanical interlocking mechanism reduces the flowability by resisting the free-flow of the powder particles relative to each other (Figure 5-24(b)), the contact surface reduction mechanism may improve the flowability (Figure 5-24(c))(Jallo et al., 2011). Compared to raw host powder, the inter-particle tangling caused by agglomerated guest particles leads to the enhanced flow resistivity. Conversely, homogenous distribution and de-agglomeration of guest particles lowers the contact surface area required for the movement of guest-decorated host particles (particle 1) from position (I) to position (II) relative to another particle assumed fixed (particle 2), as shown in Figure 5-24(d). By reducing inter-particle friction and adhesion forces, this mechanism can improve flowability (Jallo et al., 2011; H. Y. Xie, 1997; J. Yang et al., 2005). The reduced flowability in powder processed with 10G-force could be due to dominance of mechanical interlocking mechanism caused by agglomerated guest nano-particles on host surface. However, as the gravitational force increased, the flowability showed a progressive enhancement, reaching its highest point at 80G. When having nano-sized guest particles homogeneously deposited on the host, the artificially generated nano-scale roughness can enhance the flowability (J. Yang et al., 2005). This could be attributed to contact surface reduction combined with the lack of active mechanical interlocking sites in such alloy powders.

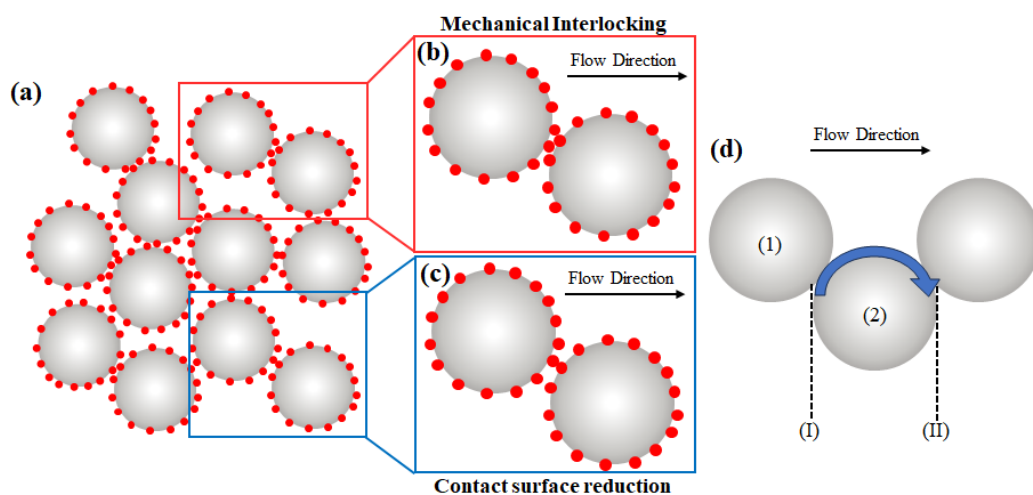


Figure 5-24 Schematic illustration of (a) an overview of guest-decorated host particles; (b) and (c) close view of selected regions showing mechanical interlocking and contact surface reduction, respectively; and (d) the contact area of two host powder particles when flowing relative to each other.

To illustrate the influence of guest-particle size on minimizing the attractive force between powders, $F_{vdW,H-G}$ was calculated. This calculation was performed for a nominal surface area coverage of 10% across three different d_{50} as shown in Figure 5-25. The results indicate the attractive force between host particles increases with their size but decreases as the size of guest particles increases. The increased separation between host particles due to the presence of guest particles eventually leads to a minimum in the attractive force. The extent of the reduction in effective adhesion depends on the size of the guest particles, with the optimal size for minimizing adhesion also being dependent on the size of the host particles (J. Yang et al., 2005). Beyond this point, the nanoparticle coating begins to significantly contribute to the overall attractive force, and the interactions between guest and host particles intensify. Consequently, the total adhesive force increases and becomes less dependent on the size of the host particles in the case of larger guest particles. Zhu et al. (X. Zhu et al., 2017) explore the influence of guest-particle agglomeration on the efficacy of adhesion reduction. They ascertain nanoparticle distribution is dependent upon the intrinsic material characteristics and the coating methodology. The guest-particle agglomeration results in an increase in effective particle size and a reduction in surface area coverage, consequently enhancing interparticle cohesion. The objective of the coating is thus to facilitate the deposition of minimally sized guest-particles onto the host surface to maximize flow properties.

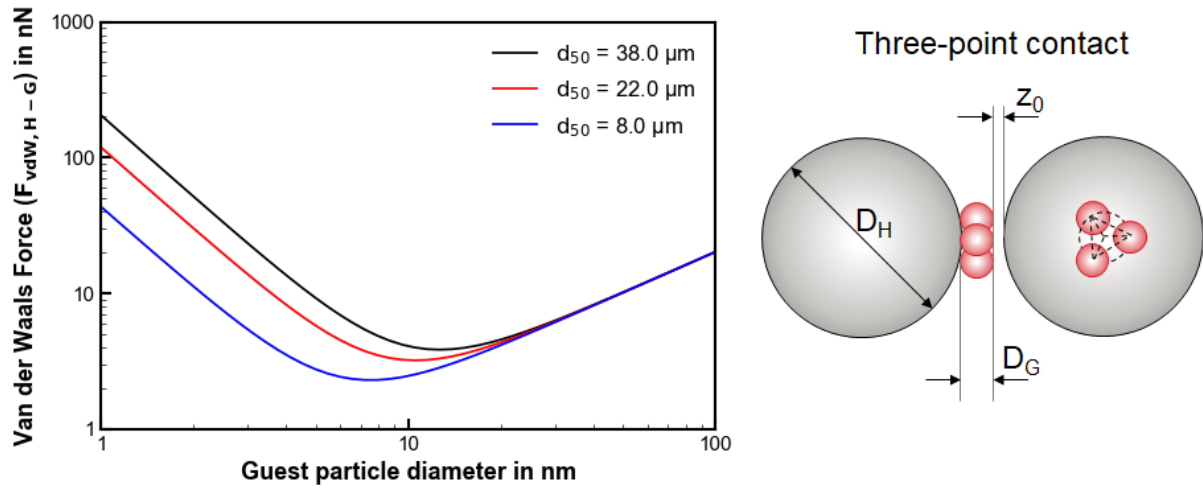


Figure 5-25 Guest-particle size effect on attraction force according to the three-point contact model ($SAC_{nom}=10\%$, $z_0=0.4 \cdot 10^{-9}m$, $A_{Boron}=6.23 \times 10^{-20} J$, $A_{Ti6Al4V}=2.668 \times 10^{-19} J$) (X. Liu et al., 2009; Tolias, 2020).

5.5.4 Effect of RAM Conditions on Oxide Layer Thickness

The trends in oxide layer thickness of host material and its boron-decorated counterparts under different RAM process conditions reveal the impact of mechanical processing on surface characteristics. Increasing gravitational acceleration leads to a reduction in oxide layer thickness due to intensified mechanical forces. These forces enhance mechanical interaction, promoting more effective disruption and removal of the oxide layer, resulting in a thinner oxide

layer with increased mechanical energy input. The surface oxide layer influenced by RAM processing significantly affects the properties and behaviour of powders. Higher oxide content increases the full melting temperature, preventing individual molten powders from contacting each other at the liquidus temperature. This reduced permeability hinders the formation of an integrated melt pool due to high interfacial energy and limited wetting between the melt and surrounding oxides. Solid oxides may still maintain the layer on the molten powder surface. According to the Young-Laplace equation (Ibach, 2006), the capillary pressure p_c of the individual powder melt flow through surrounding oxides is described as $p_c = 2\gamma \cos\theta / r_c$ where γ is the interfacial energy, r_c is the effective radius of the interface, and θ is the wetting angle. Surface oxide concentration influences the effective radius of the interface, with unoxidized powder surface between oxide patches. Higher oxide concentration results in greater coverage of oxide patches and a smaller pure metal surface area, making it harder for high-oxygen molten powder to permeate and integrate into a single melt pool due to reduced gap dimensions. However, the wettability of steel melt on surrounding oxide increases with rising temperature (HUMENIK & KINGERY, 1954), reducing capillary pressure for powder melt permeating the surface oxide. To compensate for reduced permeability from higher oxide concentration, further temperature increase is needed for melt pool integration in high-oxygen powder melting. Figure 5-26 illustrates the effect of surface oxides on the powder melting process. Large oxide patches on high-oxygen powder form a ceramic cage, retaining molten metal due to limited wetting of the metal melt. Higher temperatures are needed to assist melt integration. In contrast, low-oxygen powder melts form an integrated pool at the liquidus temperature. Balling defects [46,47] caused by inappropriate fusion parameters, may also appear with the surface oxide-induced cage effect in PBF-LB/M. The oxide layer on molten powder maintains the spherical shape due to high surface tension and poor substrate wetting. Due to limited melting time from high scan speed in PBF-LB/M, much higher heating temperatures are required to eliminate balling behaviour induced by the cage effect.

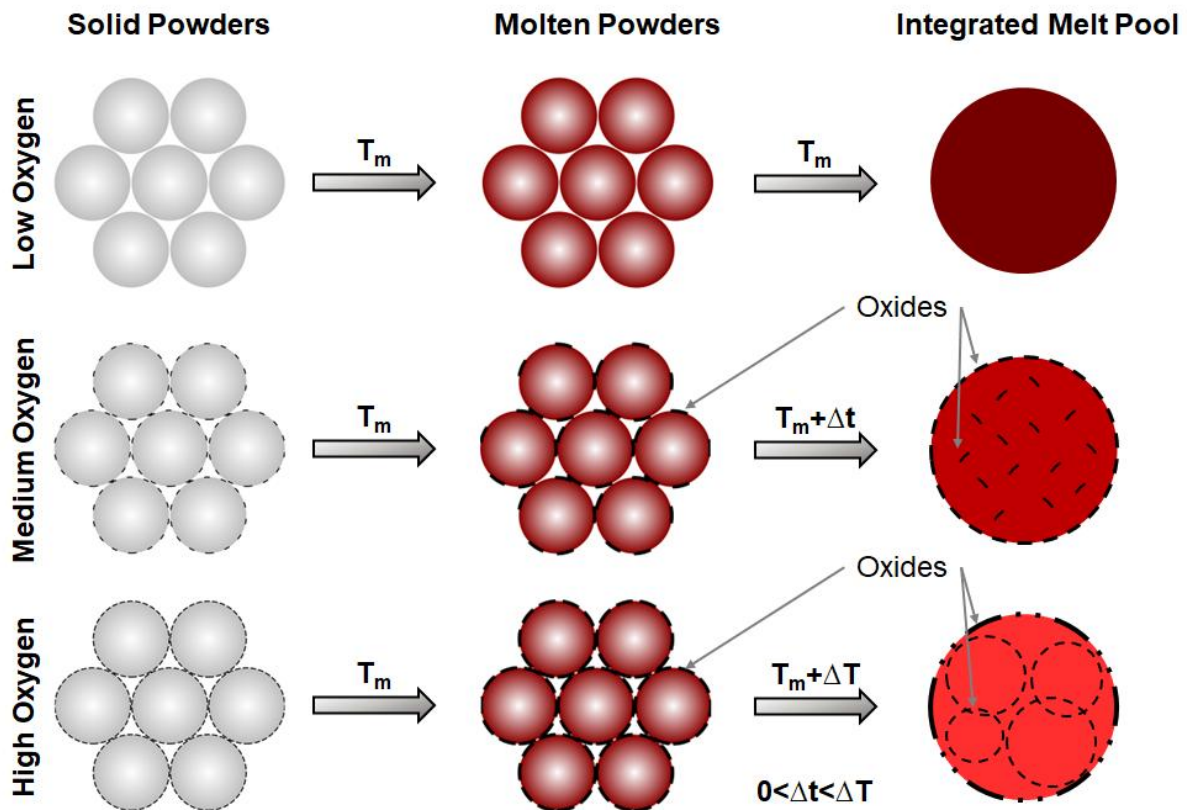


Figure 5-26 A schematic showing the cage effect of surface oxide layer, requiring higher temperatures to improve wetting, reduce interfacial tension, and lower capillary pressure for forming a single melting pool.

5.6 Conclusion

This study investigated the properties and performance of 0.1 wt.% boron (guest)/Ti6Al4V (host) composite powders produced by a dry-based Resonant Acoustic Mixing (RAM) process, specifically for PBF-LB/M applications. Comprehensive characterization included morphology, particle size distribution, nanoparticle coating efficiency, flowability, laser reflectivity, and surface oxide analysis. The primary conclusions are:

- Nanoparticle dispersion and powder homogeneity strongly depended on RAM gravitational acceleration (G-force). The best dispersion and uniform size distribution occurred around 80G.
- Coating quality depended on guest particle size, stiffness, and RAM intensity. Soft, micron-sized particles effectively adhered at lower G-forces (~30G), while harder micron-sized particles tended to bounce off, requiring higher de-agglomeration. In contrast, nanosized guest particles consistently adhered well at all mixing intensities tested.

- Higher mixing intensities improved nanoparticle coating quality by effectively reducing agglomeration. However, nanosized particle attachment was less sensitive to changes in mixing intensity compared to larger particles.
- The coating index (K_c) and de-agglomeration index (K_d) accurately predicted mixing performance. Higher K_c values (>1) indicated strong adhesive mixing and optimal coating quality, while K_d values ($0 < K_d < 1$) reflected efficient nanoparticle dispersion.
- Powder flowability initially deteriorated at intermediate G-forces due to increased particle interlocking from nanoparticle agglomeration but significantly improved at higher intensities due to enhanced nanoparticle dispersion and reduced inter-particle friction.
- Laser reflectivity decreased as mixing intensity increased up to 80G, correlating with improved surface roughness and nanoparticle adhesion. Beyond 80G (at 100G), reflectivity slightly increased, suggesting an optimum mixing intensity exists for surface quality.
- Increasing G-forces progressively reduced the surface oxide thickness, achieving minimal oxide contamination at the highest intensity (100G). Thinner oxide layers are beneficial for improved laser absorption and enhanced powder performance in PBF-LB/M.

Overall, the RAM technique demonstrated significant advantages for producing high-quality composite powders tailored for PBF-LB/M. Considering microstructural integrity, flowability, surface properties, and overall powder performance, 50G was identified as the optimal mixing intensity, underscoring RAM's potential as an advanced powder preparation method for additive manufacturing applications.

CHAPTER 6

BORON-INDUCED MICROSTRUCTURAL MANIPULATION OF Ti6Al4V FABRICATED BY PBF-LB/M

6.1 Introduction

One of the difficulties with PBF-LB/M is replicating microstructures comparable to those produced by conventional methods. PBF-LB/M can often result in unwanted characteristics, such as oversized grains and columnar grain formations (M. J. Bermingham et al., 2019). These issues can significantly compromise the structural integrity of a part, leading to reduced tensile and yield strength (Attar et al., 2019). PBF-LB/M processes are characterized by extremely high thermal gradients and rapid cooling rates, often leading to non-equilibrium solidification (Jinschek et al., 2022). Additionally, the layer-by-layer deposition approach introduces significant anisotropy in mechanical properties, with notable variations between the build and transverse directions (Carroll et al., 2015). During the process of forming parts from metal powders, grains begin to nucleate within the melt pool from the surface of the prior layer. These grains can grow into well-ordered structures, such as columnar formations, which can negatively impact the mechanical performance of the part. This can lead to hot tearing along the boundaries of the columnar grains (Todaro et al., 2020) and also increase the likelihood of corrosion (Ralston & Birbilis, 2010).

One strategy to address this issue involves adding small quantities of elements that encourage grain refinement. It is widely understood that heterogeneous nucleation relies on a combination of nucleation sites and solute effects (M. J. Bermingham, McDonald, Dargusch, & St.John, 2008). Nuclei that solidify at a higher temperature than the surrounding metal or alloy act as seeds for crystallization as the material cools. At the same time, the presence of solute can cause constitutional undercooling. If this undercooled region forms rapidly in front of the solidifying interface, it can quickly induce heterogeneous nucleation, thereby reducing the grain size in the final structure. The solute's capacity to cause constitutional undercooling is often measured by the growth restriction factor, Q . To encourage heterogeneous nucleation in the melt pool during PBF-LB/M, it is crucial to control grain growth since parts are built layer by layer. As new layers are added, re-heating can lead to grain enlargement, which can be avoided through Zener pinning mechanism. This process involves the formation of a stable second phase at the grain

boundaries, preventing growth (Tamirisakandala & Miracle, 2012). Building on insights gained from traditional powder metallurgy, incorporating various nanostructured additives or modifiers can enhance the microstructure of metal components made via PBF-LB/M during the fabrication process, eliminating the need for extra post-processing like thermal treatments after fabrication (Chao et al., 2021).

Boron in titanium alloys plays a multifaceted role, particularly in additive manufacturing. It effectively induces constitutional supercooling due to its high growth restriction factor in titanium, one of the highest reported so far (M. J. Bermingham, McDonald, Dargusch, & St.John, 2008). In regions where the boron content surpasses the eutectic threshold, primary TiB crystals form, serving as nucleation points for titanium. The eutectic process generates TiB nanowhiskers that tend to migrate toward the grain boundaries of titanium (Y. Hu, Cong, et al., 2018; Y. Hu, Ning, et al., 2018). This prevents further grain growth during reheating through a mechanism called Zener pinning. The inclusion of boron could potentially encourage a transition from columnar to equiaxed grains (CTE), refine the grain structure, and address some of the current challenges related to microstructure control in additive manufacturing processes (M. J. Bermingham et al., 2019). The effectiveness of boron in altering the microstructural characteristics of titanium and its alloys, even when added in trace amounts, is crucial due to the strict guidelines set by ASTM F2924 (ASTM International, 2021) for the composition of Ti6Al4V components produced via PBF. While specific tolerances are specified for elements like Al, V, Fe, O, C, N, H, and Y, any other elements are limited to a maximum of 0.1 wt.% individually, with a cumulative limit of 0.4 wt.%. This restriction implies that efforts to modify the microstructure "within standard" must rely on the addition of elements at trace levels (M. J. Bermingham et al., 2018). However, identifying the "ideal" or "necessary" amount of boron in additively manufactured titanium and its alloy parts remains a challenging area of research. For instance, Zhang et al. (K. Zhang et al., 2019) found that even small amounts of boron (≤ 1.0 wt.%) were enough to trigger the columnar-to-equiaxed transition of prior- β grains, eliminate unwanted α phases such as grain boundary α , and encourage the formation of fine α laths with a lower aspect ratio and weakened texture. However, Zhang et al. (K. Zhang et al., 2019) also observed that increasing the boron content led to a gradual decrease in ductility. In their work, they recommended an addition of 0.05 wt.%B for achieving an optimal balance of tensile properties. On the other hand, He et al. (Y. He et al., 2019) employed a powder-free PBF-LB/M method—where laser scanning was done on arc-melted buttons—to explore the combination of Ti6Al4V and boron across a broad composition range, extending up to 10 wt.%B. They experimented with 14 different laser power and scan speed settings for each composition, resulting in 70 single-track scans. From this extensive analysis, He et al. (Y. He et al., 2019) concluded that boron levels between 2 and 5 wt.% are promising for fabricating Ti6Al4V composite parts using PBF-LB/M. This range offered a substantial processing window, produced a stable melt pool size comparable to unmodified Ti6Al4V, and led to a favourable microstructure featuring a TiB network with submicron spacing.

The aim of this chapter is to explore the role of a 0.1 wt.%B addition in refining the microstructure of Ti6Al4V components produced via PBF-LB/M additive manufacturing. By leveraging high growth restriction factor of boron in titanium, this study intends to induce in-situ grain refinement, potentially transforming the columnar grain structure to a more desirable equiaxed form. The chapter aims to assess how this boron-induced microstructural manipulation can address common challenges in PBF-LB/M, such as oversized grains and anisotropy, while still adhering to the stringent composition requirements outlined by ASTM F2924 (ASTM International, 2021). Ultimately, the study seeks to provide insights into optimizing mechanical properties and enhancing the quality of PBF-LB/M-manufactured Ti6Al4V parts through trace element modification.

6.2 Influence of Process Parameters on the Densification

Based on the laser glazing experiments presented in Chapter 4, six processing parameters were selected for detailed analysis of in-situ grain refinement during the PBF-LB/M process. Cuboidal samples with a dimension of $7 \times 7 \times 7 \text{ mm}^3$ were fabricated atop 2 mm-high support structures, comprising approximately 233 layers with a fixed layer thickness of 30 μm . The relative density of each PBF-LB/M sample was systematically quantified through complementary Archimedes' principle and metallographic pore area fraction analysis (Dilip et al., 2017). The relative density was calculated in relation to the reference density value established as the specific mass of the alloy, 4.43 g/cm^3 . The scan parameters were varied by changing the exposure time, ranging from 30 to 200 μs , while maintaining constant laser power (150 W), point distance (30 μm), hatch spacing (65 μm), and layer thickness (30 μm). Consequently, the corresponding line energy density (LED)—defined as the ratio of laser power (P) to scan speed (v)—ranged from 0.15 J/mm for the shortest exposure time of 30 μs to 1.00 J/mm at the longest exposure time of 200 μs . Figure 6-1 shows the macrostructures taken from the longitudinal sections of samples fabricated by PBF-LB/M using six different laser scan parameters and thus different line energy densities. The scan parameters were varied by changing the exposure time while keeping all other variables constant. The black areas in the images indicate the porosities present in the longitudinal planes of the fabricated samples. The unmodified Ti6Al4V samples (Figure 6-1(a) – (f)) show a progressive increase in pore density with increasing exposure times, i.e. higher line energy densities increasing from 0.15 J/mm at 30 μs exposure to 1.00 J/mm at 200 μs exposure, with the most pronounced pore density observed at 0.60 J/mm at the 120 μs exposure time (Figure 6-1(d)) and at 0.75 J/mm at the 150 μs exposure time (Figure 6-1(e)) (Dilip et al., 2017; King et al., 2014). At the highest LED of 1.00 J/mm at the 200 μs exposure time, however, a noticeable increase in relative density occurred, corresponding to a reduction in pore density as seen in Figure 6-1(f). The introduction of amorphous boron ((Figure 6-1(a') – (f')) modified the densification of the alloy, with noticeable reduction on the density and distribution of pores compared to the unmodified samples, particularly at lower exposure times (Figure 6-1(a') – (c')) (Z. Zhou et al., 2021). However, within these amorphous boron-modified samples, the pore density was highest at 120 μs (Figure 6-1(d')) and decreased with further increases in exposure time, as observed in 150

μs and 200 μs case (Figure 6-1(e')-(f')). The samples modified with crystalline boron (Figure 6-1(a'') – (f'')) demonstrate a significant reduction in pore density across all exposure times when compared to their unmodified and amorphous boron-modified counterparts. The macrostructure appeared more uniform and stable, with fewer pores observed overall (Attar, Bönisch, Calin, Zhang, Zhuravleva, et al., 2014). At 120 μs (Figure 6-1(d'')), the samples showed a relatively low density of pores, which further decreased at 150 μs (Figure 6-1(e'')) and 200 μs (Figure 6-1(f'')), indicating an improvement in relative density with increasing exposure time. This trend indicated the crystalline boron modification resulted in a more stable and higher-quality macrostructure, particularly at higher exposure times, with a noticeable reduction in pore density, leading to a more pore-free alloy.

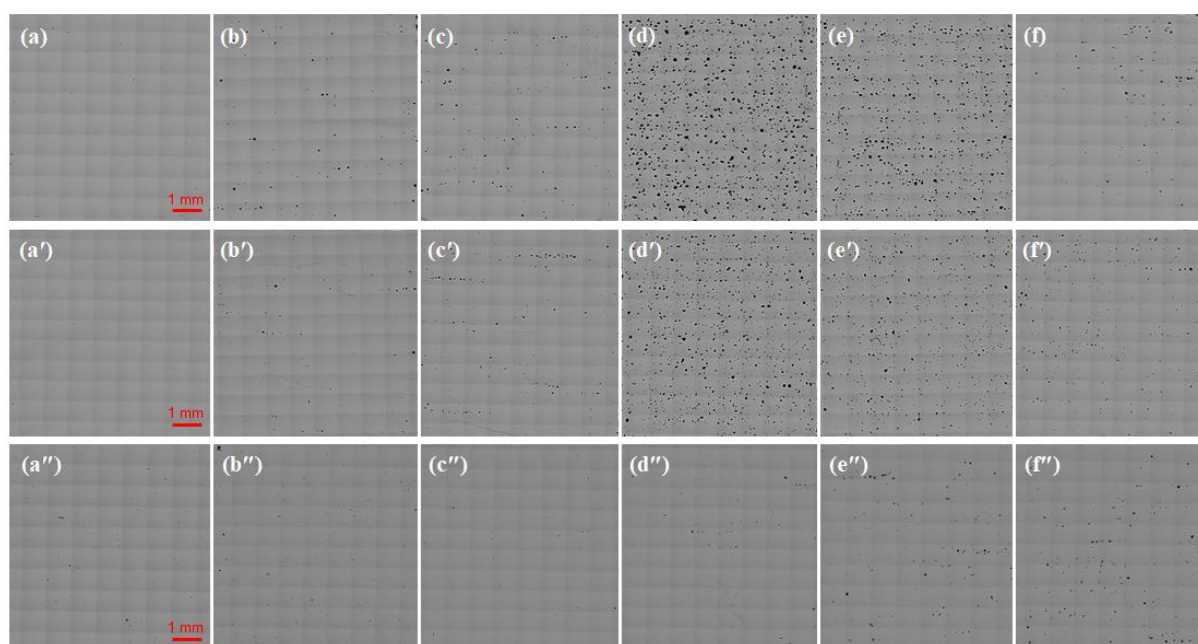


Figure 6-1 Stitched OM images of Ti6Al4V and 0.1 wt.%B-modified Ti6Al4V alloys processed using different laser scan parameters. Images (a) to (f) represent Ti6Al4V alloy processed with 150W and exposure times ET30, ET60, ET90, ET120, ET150, and ET200, respectively. Images (a') to (f') show the corresponding microstructures for the alloy modified with amorphous boron under the same exposure conditions, while images (a'') to (f'') illustrate the microstructures for the alloy modified with crystalline boron under identical exposure parameters. The scale bar in each set of images represents 1mm.

The relative density of Ti6Al4V and 0.1 wt.%B-modified Ti6Al4V alloys was measured by both Archimedes' principle and pore area fraction based on OM images are compared in Figure 6-2. A red dashed line indicates a target density level of 99%, suggesting minimal or no impact on mechanical properties, assuming the presence of nearly spherical, low aspect ratio pores (Yusuf et al., 2017). The relative density measured by the OM method was generally higher than that obtained using Archimedes' method. However, the Archimedes' method was considered more reliable since it accounts for the entire sample volume, whereas the OM

method based on pore area fraction relies on discrete cross-sections, which may not accurately reflect the overall porosity of the sample. The standard deviation of the relative density measurements using Archimedes' method is less than 0.28%, which is notably lower compared to the standard deviation obtained from optical microscopy (OM), which is less than 1.81%. This difference is particularly evident in samples with lower densities. Both methods showed that the relative density of all samples generally remained close to 99% across most linear energy densities, with a noticeable drop occurring in the mid-range value of 600 J/m for all samples. In Figure 6-2(a), as measured by Archimedes' principle, samples produced with Ti6Al4V alloy without boron modification exhibited the most pronounced decrease in relative density at intermediate LEDs, reaching a minimum near 95%. In contrast, the samples produced by amorphous and crystalline boron-modified Ti6Al4V alloy showed an improvement in relative density across the LED spectrum, with the crystalline boron-modified samples maintaining the highest relative density, particularly at higher LEDs. Similarly, Figure 6-2(b), displaying relative density based on pore area fraction from OM images, corroborated these findings, although with slightly lower relative density values, particularly in the mid-LED range. The crystalline boron-modified samples consistently exhibited the highest relative density across the LED range. The amorphous boron-modified samples also showed improved relative densities compared to the unmodified Ti6Al4V, although to a lesser extent than the crystalline boron-modified samples. Moreover, the pores observed in the samples were predominantly small and spherical, primarily located within the melt pools. This distribution suggests that the pores were likely caused by gas entrapment due to high laser energy, turbulent melt pool dynamics, the vaporization of low melting point elements (B. Zhang et al., 2017), or gas-induced voids present in the powder feedstock (L. Hao et al., 2009).

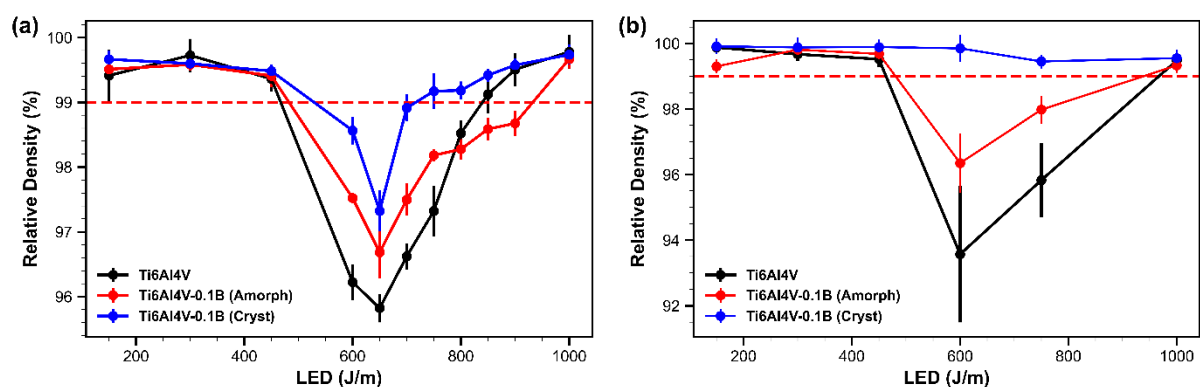


Figure 6-2 Relative density of Ti6Al4V and 0.1 wt.%B-modified Ti6Al4V alloys processed with 150W at different laser scan parameters. (a) Relative density measured using Archimedes' principle; and (b) relative density based on pore area fraction from OM images.

To optimize porosity at the higher power setting of 150 W, additional experiments using a reduced laser power of 100 W using cuboidal samples measuring $7 \times 7 \times 7 \text{ mm}^3$ built atop 2 mm-high support structures. Each sample comprised approximately 233 layers, with constant layer thickness of 30 μm , hatch spacing of 65 μm , and point distance of 30 μm . The exposure time

was systematically varied at 120 μs , 180 μs , 225 μs , 300 μs , and 450 μs , corresponding to line energy densities (LED) of approximately 0.40, 0.60, 0.75, 1.00, and 1.50 J/mm, respectively. This approach was designed to explore the influence of lower power on the microstructural characteristics and porosity of the samples, with the aim of achieving a more controlled and uniform material quality. Figure 6-3 illustrates macrostructures taken from the longitudinal sections of samples processed using different laser scan parameters, with power set at 100 W. The unmodified Ti6Al4V samples (Figure 6-3(a) – (e)) showed a significant decrease in pore density as the exposure time increases, and thus higher line energy density, reflecting the well-known reduction of lack-of-fusion defects and enhanced melt-pool stability at elevated LED (Dilip et al., 2017; King et al., 2014). The highest pore density appeared at the shortest exposure time of 120 μs with LED of 0.40 J/mm (Figure 6-3(a)), steadily diminishing with longer exposure times. By the longest exposure time of 450 μs , corresponding to the highest LED of 1.50 J/mm (Figure 6-3(e)), porosity was substantially reduced, demonstrating a progressive improvement in relative density. In the samples modified with amorphous boron (Figure 6-3(a') – (e')), a similar trend was observed. The pore density was highest at 120 μs (Figure 6-3(a')) and decreased with increasing exposure time, as seen in the 180 μs to 450 μs range (Figure 6-3(b') – (e')), although the overall relative density remained lower than that of the unmodified alloy across all exposure times, consistent with the role of in situ TiB precipitation in refining grains and stabilising the melt pool (Z. Zhou et al., 2021). The crystalline boron-modified samples (Figure 6-3(a'') – (e'')) exhibited the most significant reduction in pore density across all exposure times when compared to both unmodified and amorphous boron-modified counterparts. These samples display a more uniform and stable microstructure with fewer pores, especially as exposure time increases, in line with previously reported improvements in densification via heterogeneous nucleation by TiB particles (Attar, Bönisch, Calin, Zhang, Zhuravleva, et al., 2014). Notably, the crystalline boron-modified samples processed at 120 μs (Figure 6-3(a'')) already showed a relatively low pore density, continuing to decrease significantly through to 450 μs (Figure 6-3(e'')).

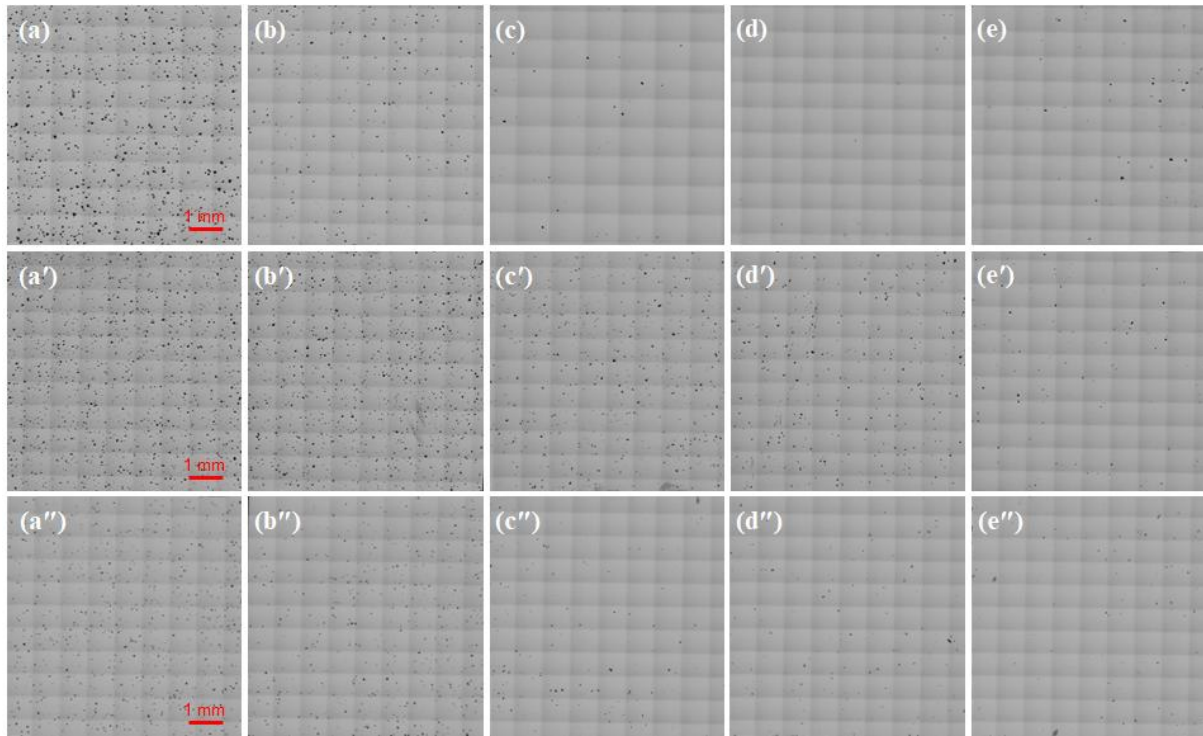


Figure 6-3 Stitched OM images of Ti6Al4V and 0.1 wt.%B-modified Ti6Al4V alloys processed using different laser scan parameters. Images (a) to (e) represent Ti6Al4V alloy processed with 100W and exposure times ET120, ET180, ET225, ET300, and ET450, respectively. Images (a') to (e') show the corresponding microstructures for the alloy modified with amorphous boron under the same exposure conditions, while images (a'') to (e'') illustrate the microstructures for the alloy modified with crystalline boron under identical exposure parameters. The scale bar in each set of images represents 1mm.

Figure 6-4 compares the relative density of Ti6Al4V and 0.1 wt.% B-modified Ti6Al4V alloys processed at 100W using various laser scan parameters, measured by both Archimedes' principle (Figure 6-4(a)) and pore area fraction from OM images (Figure 6-4(b)). The results showed the relative density generally increased with higher line energy densities (LEDs) for all sample types. In Figure 6-4(a), the relative density measured by Archimedes' principle showed crystalline boron-modified samples consistently achieved the highest relative density, followed by unmodified and amorphous boron-modified Ti6Al4V samples. Notably, after 800 J/m, the relative density for all samples increased to 99% or beyond, indicating effective densification at higher energy inputs. This trend was mirrored in Figure 6-4(b), where the relative density based on pore area fraction from OM images confirmed crystalline boron-modified samples maintained superior density across all LEDs. The unmodified Ti6Al4V samples also demonstrated improved densities compared to the amorphous boron-modified counterparts, though slightly lower than those achieved with crystalline boron.

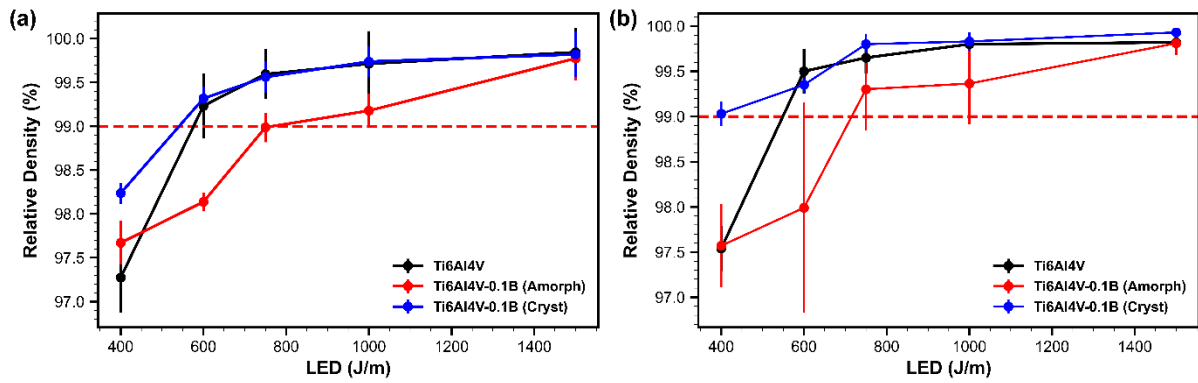


Figure 6-4 Relative density of Ti6Al4V and 0.1 wt.%B-modified Ti6Al4V alloys processed with 100W at different laser scan parameters. (a) Relative density measured using Archimedes' principle; and (b) relative density based on pore area fraction from OM images.

6.3 Influence of Process Parameters on the Hardness

Figure 6-5 presents the hardness maps of Ti6Al4V and 0.1 wt.%B-modified Ti6Al4V alloys processed with 150W at varying exposure times. In the figure, the red dotted lines highlight the hardness distribution in the top region of each sample, and the black dotted lines indicate the hardness distribution in the bottom region of each sample. Hardness maps in Figure 6-5(a – (d)) illustrate the hardness distribution in the unmodified Ti6Al4V alloy at exposure times of 30 μ s, 60 μ s, 90 μ s, and 120 μ s, respectively. The hardness distribution was relatively uniform across the maps, but with a clear gradient from top to bottom, reflecting the effect of differing cooling rates between the upper and lower melt-pool surfaces (Frazier, 2014). The top regions of the samples consistently exhibited higher hardness values, which gradually decreased toward the bottom regions—a phenomenon commonly observed in PBF-LB/M Ti6Al4V due to rapid solidification of the top layers (Majumdar et al., 2019). This gradient indicated a difference in cooling rates or thermal histories between the top and bottom regions during processing, leading to variations in hardness. Additionally, while the overall hardness remained consistent across different exposure times, subtle variations in the distribution pattern suggest that exposure time may influence the extent of hardness variation within the sample. In the amorphous boron-modified samples (Figure 6-5(a') – (d')), the hardness distribution exhibited greater variability compared to the unmodified alloy. In all the amorphous boron-modified samples, a noticeable gradient in hardness was observed between the top and bottom regions of the samples. The top regions consistently exhibited higher hardness values compared to the bottom regions. This difference was most pronounced in the samples processed with 30 μ s (Figure 6-5(a')) and 60 μ s (Figure 6-5(b')) samples. As the exposure time increases to 90 μ s (Figure 6-5(c')) and 120 μ s (Figure 6-5(d')), a trend of overall reduced hardness was observed, particularly in the middle and bottom sections—consistent with the stabilising effect of TiB precipitates on microstructural evolution (Z. Zhou et al., 2021). The sample produced with 120 μ s (Figure 6-5(d')) showed a marked decrease in hardness across the middle region. This decrease in hardness could be indicative of a phase transformation or other microstructural changes.

Hardness maps in Figure 6-5(a'') – (d'') display the hardness mapping of crystalline boron-modified alloys processed at different exposure times. The hardness distribution was more uniform across these samples compared to the other two alloy systems. The top regions like the other alloy systems showed higher hardness values. In the samples produced with 30 μ s (Figure 6-5(a'')) and 60 μ s (Figure 6-5(b'')), the hardness map showed a significantly high hardness in the top and middle regions, with only a gradual decrease towards the bottom regions. As exposure time increases to 90 μ s (Figure 6-5(c'')), the hardness remained relatively high and evenly distributed, with minimal reduction in the bottom sections. The sample produced with 120 μ s (Figure 6-5(d'')) maintained a strong hardness profile across the top section but decreased significantly in the middle and bottom regions—mirroring reported improvements in uniformity and thermal stability conferred by in situ TiB whiskers (Attar, Bönisch, Calin, Zhang, Zhuravleva, et al., 2014).

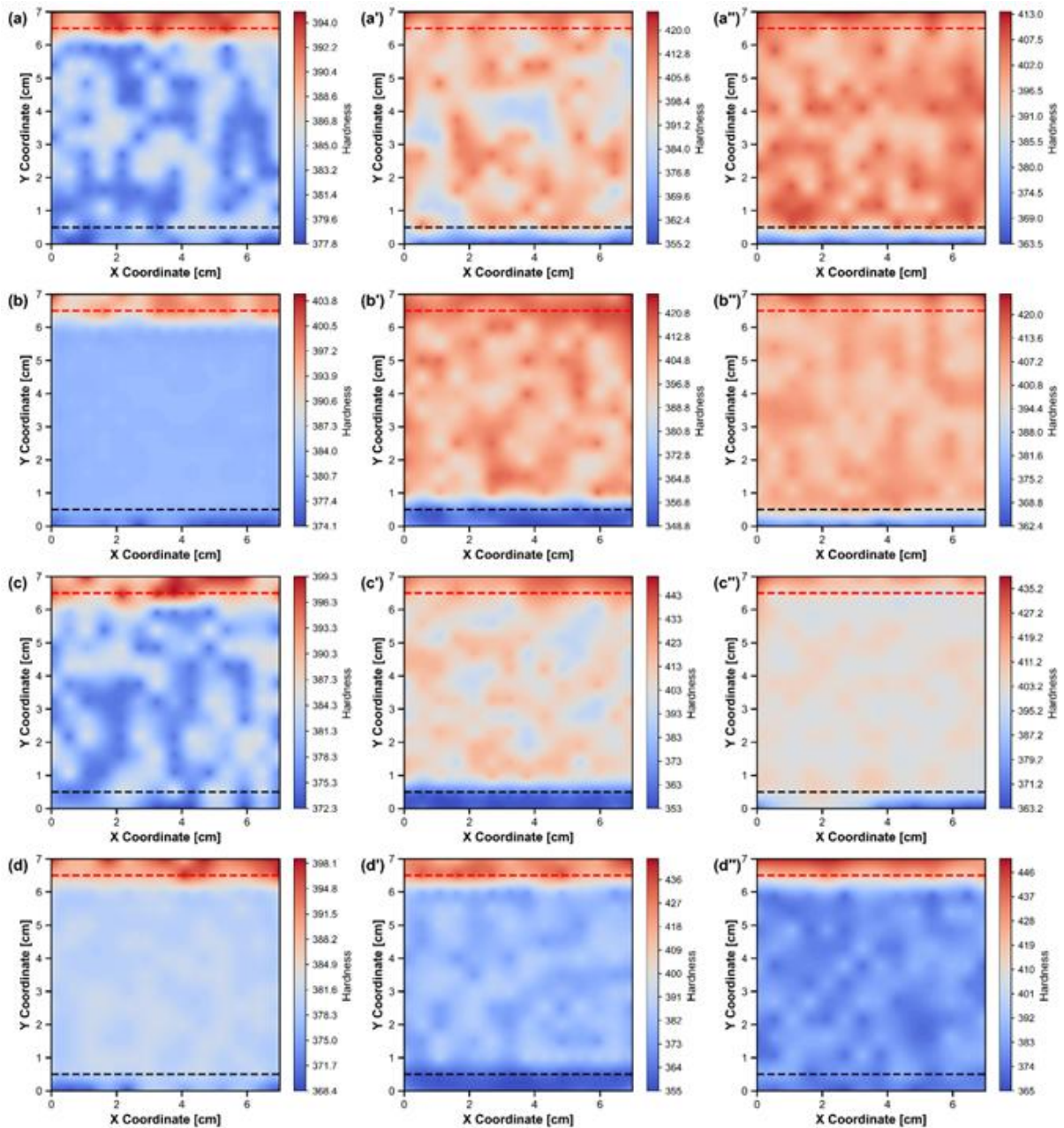


Figure 6-5 Hardness mapping of Ti6Al4V and 0.1 wt.%B-modified Ti6Al4V alloys processed with 150W at different laser scan parameters. Maps (a) to (d) represent Ti6Al4V alloy processed with exposure times ET30, ET60, ET90, and ET120, respectively. Images (a') to (d') show the corresponding hardness map for the alloy modified with amorphous boron under the same exposure conditions, while images (a'') to (d'') illustrate the maps for the alloy modified with crystalline boron under identical exposure parameters.

Table 6-1 presents the average hardness values for the bottom, middle, and top regions of Ti6Al4V and 0.1 wt.% B-modified Ti6Al4V alloys processed with 150W at different laser scan parameters. The hardness distribution within the unmodified Ti6Al4V samples exhibited a consistent trend of increasing hardness from the bottom to the top regions across all exposure

times. Ti6Al4V sample processed with 30 μ s exposure time showed an average hardness of 379HV in the bottom region, which increased to 392HV in the top region. A similar pattern was observed for the 60 μ s exposure time condition, where hardness values increased from 376HV in the bottom to 394HV in the top region. As the exposure time increases to 90 μ s, the top region maintained a higher hardness of 392HV, despite slight decreases in the bottom (375HV) and middle (381HV) regions. At the longest exposure time of 120 μ s, the hardness trend continued with a bottom region hardness of 372HV, middle region hardness of 380HV, and top region hardness of 393HV. The amorphous boron-modified samples exhibited higher hardness in the top regions across all exposure times, similar to the unmodified samples, but with greater variability in the middle and bottom regions, particularly at longer exposure times. At 30 μ s exposure time, hardness in the amorphous boron-modified samples increased from 358HV in the bottom region to 408HV in the top region. Similar trends were observed at 60 μ s and 90 μ s, where hardness generally rose from the bottom to the top, with the middle region showing relatively stable values around 401HV and 407HV, respectively. However, at exposure time of 120 μ s, a significant difference was observed in the middle region, where hardness dropped to 381HV, contrasting with the consistently higher values seen in other exposure times. This drop indicates a notable deviation in the microstructural integrity at 120 μ s, while the top region maintained a high hardness of 422HV, and the bottom remained lower at 356HV. The crystalline boron-modified samples demonstrated a more consistent and higher hardness distribution across all regions compared to the unmodified and amorphous boron-modified samples. At 30 μ s, average hardness of samples increased from 366HV at the bottom to 407HV at the top, with the middle at 399HV. This trend continued at 60 μ s, with the middle region reaching 403HV. At 90 μ s, the middle slightly increased to 405HV. However, at 120 μ s, the middle region showed a more significant drop to 382HV, while the top remained high at 419HV.

Table 6-1 Average hardness values for different regions of unmodified and 0.1 wt.%B-modified Ti6Al4V alloys processed with 150W at different laser scan parameters.

Parameter	Region	Ti6Al4V	Ti6Al4V-0.1B (Amorph)	Ti6Al4V-0.1B (Cryst)
P150 ET30	Bottom	379.26 $\pm$ 1.68	358.41 $\pm$ 3.12	366.19 $\pm$ 2.67
	Middle	384.66 $\pm$ 3.56	401.08 $\pm$ 8.93	399.99 $\pm$ 6.14
	Top	392.43 $\pm$ 2.43	408.41 $\pm$ 4.39	407.65 $\pm$ 3.85
P150 ET60	Bottom	376.25 $\pm$ 2.30	356.14 $\pm$ 5.33	366.08 $\pm$ 3.54
	Middle	386.59 $\pm$ 3.09	404.41 $\pm$ 8.13	403.87 $\pm$ 3.96
	Top	394.49 $\pm$ 2.10	412.75 $\pm$ 6.22	415.68 $\pm$ 3.71
P150 ET90	Bottom	375.89 $\pm$ 3.42	359.86 $\pm$ 2.75	365.77 $\pm$ 2.42
	Middle	381.35 $\pm$ 3.88	407.50 $\pm$ 8.37	405.75 $\pm$ 2.94
	Top	392.97 $\pm$ 3.83	419.43 $\pm$ 6.66	419.50 $\pm$ 4.56
P150 ET120	Bottom	372.41 $\pm$ 3.67	359.72 $\pm$ 2.06	369.95 $\pm$ 4.10
	Middle	380.76 $\pm$ 0.89	381.36 $\pm$ 5.32	382.29 $\pm$ 4.86
	Top	393.48 $\pm$ 3.34	422.50 $\pm$ 6.64	419.52 $\pm$ 6.24

Figure 6-6 presents the hardness maps of Ti6Al4V and 0.1 wt.%B-modified Ti6Al4V alloys processed with 100W at varying exposure times. In the unmodified Ti6Al4V samples (Figure 6-6(a) – (e)), the hardness distribution exhibited a clear gradient from the top to the bottom, with the top regions consistently showing higher hardness values. This gradient indicates a variation in cooling rates or thermal histories across the sample height, leading to the observed hardness differences. The maps showed average hardness values generally decreased from the top to the bottom regions across all exposure times, with the top regions maintaining relatively high hardness. Additionally, the overall hardness remained consistent across different exposure times, but subtle variations in the distribution pattern was observed within the samples, implying that exposure time may influence the extent of hardness variation within the sample. In the amorphous boron-modified samples (Figure 6-6(a') – (e')), the hardness distribution across these samples showed significant variability. At shorter exposure times of 120 μ s (Figure 6-6(a')), the top and middle regions consistently exhibited higher hardness values compared to the bottom regions. However, as the exposure increased to 180 μ s (Figure 6-6(b')) and further up to 450 μ s (Figure 6-6(e')), there was a noticeable reduction of hardness value in the middle regions. The decrease in hardness in the middle regions at higher exposure times indicates potential microstructural changes or phase transformations that may be influencing the overall hardness distribution within the amorphous boron-modified samples. The hardness maps of crystalline boron-modified Ti6Al4V alloys, shown in Figure 6-6(a'') – (e'') demonstrate a similar hardness distribution like the other two alloys, with the top regions consistently exhibited higher hardness values, and it gradually decreased toward the middle and bottom regions. At shorter exposure time of 120 μ s (Figure 6-6(a'')), the hardness was relatively high and evenly distributed from the top to the middle regions, with only a slight reduction observed towards the bottom. As the exposure time increased to 180 μ s (Figure 6-6(b'')) and further up to 450 μ s (Figure 6-6(e'')), a similar pattern was observed, with the top regions maintaining strong hardness values, while the middle and bottom regions showed a more noticeable decrease. The hardness maps of crystalline boron-modified alloys revealed higher overall hardness values across all regions—top, middle, and bottom—when compared to the amorphous boron-modified counterparts. This enhanced hardness distribution could be the indication of a more refined and stable microstructure.

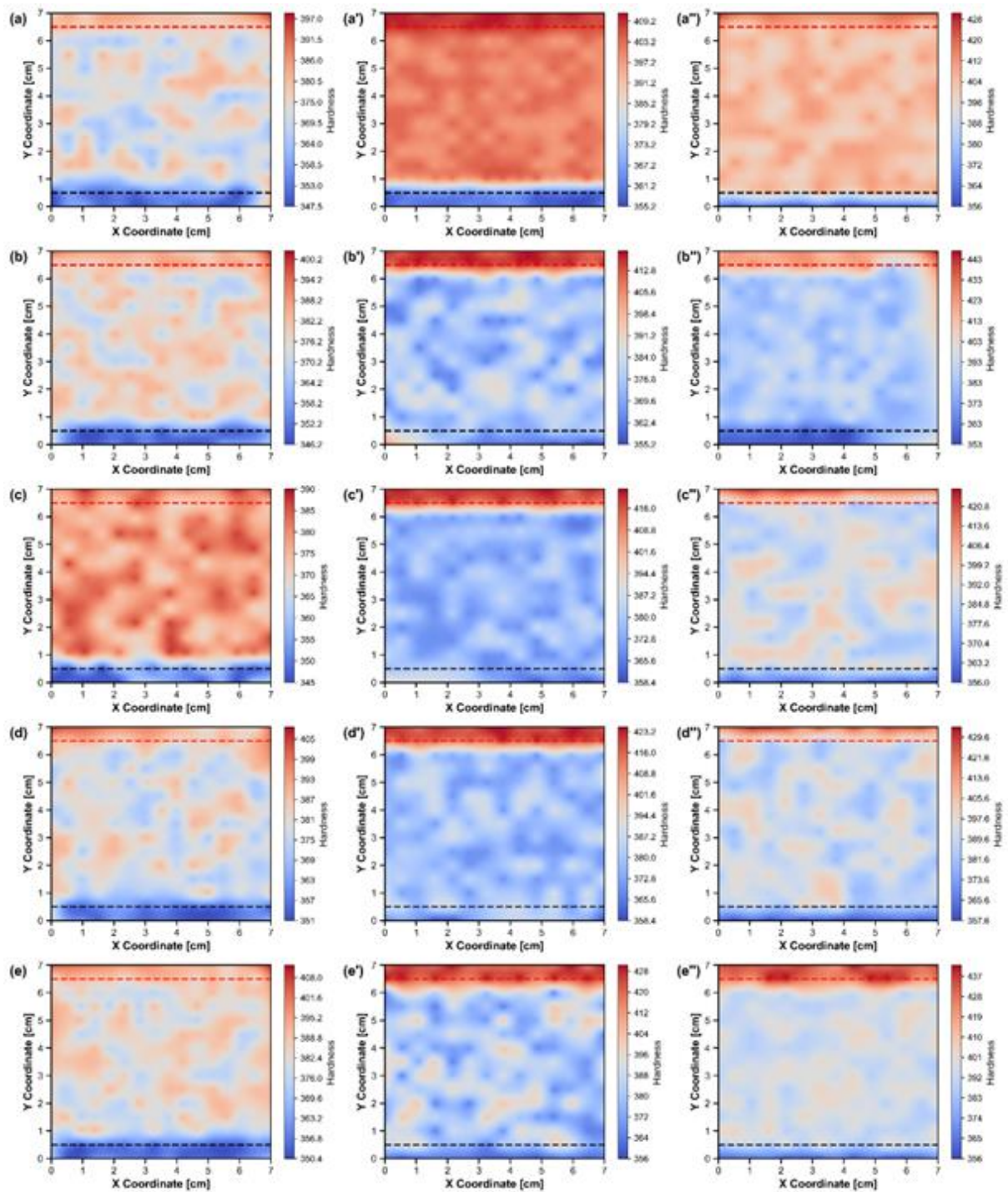


Figure 6-6 Hardness mapping of Ti6Al4V and 0.1 wt.%B-modified Ti6Al4V alloys processed with 100W at different laser scan parameters. Maps (a) to (d) represent Ti6Al4V alloy processed with exposure times ET120, ET180, ET225, ET300 and ET450, respectively. Images (a') to (d') show the corresponding hardness map for the alloy modified with amorphous boron under the same exposure conditions, while images (a'') to (d'') illustrate the maps for the alloy modified with crystalline boron under identical exposure parameters.

Table 6-2 presents the average hardness values for different regions of Ti6Al4V and 0.1 wt.%B-modified Ti6Al4V alloys processed with 100W at various exposure times. The average hardness values for the unmodified Ti6Al4V remained relatively consistent across all exposure times, with only minor variations between the bottom, middle, and top regions. For example, the top hardness values ranged from 380HV at 120 μ s to 389HV at 450 μ s, indicating stability in the hardness regardless of the exposure time. In the boron-modified samples, both amorphous and crystalline boron addition led to higher hardness values compared to the unmodified alloy. The crystalline boron-modified samples consistently exhibited the highest hardness across all regions, particularly in the top sections, where hardness reached up to 430HV at 450 μ s. Similarly, the amorphous boron-modified samples also showed increased hardness, with top region values ranging from 409HV at 120 μ s to 423HV at 450 μ s, which were higher than those observed in the unmodified samples. However, both amorphous and crystalline boron-modified samples exhibited a noticeable decrease in hardness in the middle regions after the exposure time reached 180 μ s. For example, in the crystalline boron-modified samples, the middle hardness dropped from 404HV at 120 μ s to 386HV at 180 μ s and further decreased to 396HV at 450 μ s. A similar trend was observed in the amorphous boron-modified samples, where the middle region's hardness also decreased significantly after 180 μ s, albeit at lower levels compared to the crystalline counterpart. This trend, observed in the hardness distribution maps (Figure 6-6), indicates while both amorphous and crystalline boron modifications enhance hardness, prolonged exposure times beyond 180 μ s may lead to significant reductions in hardness, particularly in the middle regions of the samples. This reduction in hardness is likely due to phase transformations occurring at these exposure times, which can alter the microstructure and lead to a less uniform distribution of hardness within the material.

Table 6-2 Average hardness values for different regions of Ti6Al4V and 0.1 wt.%B-modified Ti6Al4V alloys processed with 100W at different laser scan parameters.

Parameter	Region	Ti6Al4V	Ti6Al4V-0.1B (Amorph)	Ti6Al4V-0.1B (Cryst)
P100 ET120	Bottom	353.35 $\pm$ 3.52	361.63 $\pm$ 2.54	359.69 $\pm$ 3.06
	Middle	374.41 $\pm$ 6.14	400.72 $\pm$ 2.76	404.93 $\pm$ 4.79
	Top	380.88 $\pm$ 3.60	409.01 $\pm$ 1.52	418.38 $\pm$ 2.50
P100 ET1800	Bottom	353.90 $\pm$ 3.81	359.93 $\pm$ 2.57	360.77 $\pm$ 4.39
	Middle	375.99 $\pm$ 5.90	376.89 $\pm$ 4.32	386.86 $\pm$ 3.72
	Top	382.00 $\pm$ 3.53	412.05 $\pm$ 2.80	419.45 $\pm$ 4.11
P100 ET225	Bottom	351.62 $\pm$ 6.45	357.87 $\pm$ 2.34	360.92 $\pm$ 4.08
	Middle	378.03 $\pm$ 5.87	378.05 $\pm$ 5.98	389.81 $\pm$ 7.01
	Top	383.88 $\pm$ 3.09	415.10 $\pm$ 4.05	423.92 $\pm$ 3.44
P100 ET300	Bottom	357.47 $\pm$ 2.97	360.54 $\pm$ 1.39	361.29 $\pm$ 2.31
	Middle	380.17 $\pm$ 6.30	380.79 $\pm$ 3.79	391.22 $\pm$ 5.36
	Top	387.13 $\pm$ 4.54	417.77 $\pm$ 3.61	424.05 $\pm$ 3.66
P100 ET450	Bottom	357.03 $\pm$ 3.61	359.83 $\pm$ 2.83	362.94 $\pm$ 3.86
	Middle	382.20 $\pm$ 5.73	382.88 $\pm$ 1.37	396.49 $\pm$ 5.71
	Top	389.39 $\pm$ 4.33	423.76 $\pm$ 3.02	430.02 $\pm$ 3.23

6.4 Phase Identification

Figure 6-7(a) shows the XRD spectra of as-built unmodified, amorphous and crystalline boron-modified Ti6Al4V alloy samples processed at different exposure times namely 30 μ s, 60 μ s, 90 μ s and 120 μ s using 150W laser power, respectively. Because the α and α' -titanium phases share the same hexagonal structure and have similar lattice parameters, their diffraction peaks cannot be distinguished from each other and are therefore referred to collectively as α/α' in this study (de Formanoir et al., 2019; Zafari et al., 2019; X. Zhao et al., 2016). The unmodified Ti6Al4V specimens contained α/α' -titanium peaks only across all the different laser scan parameters, while β -titanium peaks were not detectable under these conditions. These α/α' -titanium peaks were noticeably broad, suggesting that the as-built specimens were predominantly composed of the α' -titanium phase, which has a more distorted lattice structure due to a higher solute content compared to the more stable α -titanium phase (Sallica-Leva et al., 2016; Zeng & Bieler, 2005). However, as the laser exposure time increased, the broadness of the peaks gradually decreased, although the peak positions remained almost unchanged. In the boron-modified samples, the addition of boron led to a noticeable narrowing of the α/α' -titanium peaks compared to the unmodified Ti6Al4V, indicating a more refined microstructure. The crystalline boron-modified samples, in particular, exhibited the narrowest peaks, reflecting the most refined microstructure among the samples. Furthermore, with the longest exposure time of 120 μ s, the emergence of tiny β -titanium peaks was observed, which was absent in samples processed with shorter exposure times. The presence of the β -titanium phase indicated $\alpha' \rightarrow \alpha + \beta$ phase transformation, occurring under these specific conditions, potentially due to the extended thermal exposure. The full width at half maximum (FWHM) of the main α/α' ($10\bar{1}1$) peak across different laser scan parameters is shown in Figure 6-7(b). In the unmodified Ti6Al4V samples, FWHM values were relatively higher across all exposure times, indicating a more distorted microstructure. However, FWHM values progressively decreased with increasing laser exposure time due to martensite becoming less distorted with increasing exposure times. For the boron-modified samples, the addition of boron, particularly in its crystalline form, resulted in narrower α/α' ($10\bar{1}1$) peak compared to the unmodified alloy, reflecting a more refined structure. The crystalline boron-modified samples exhibited the lowest FWHM values across all exposure times. As in the unmodified Ti6Al4V samples, increase in the exposure time from 30 μ s to 120 μ s led FWHM values to continue to decrease for both amorphous and crystalline boron-modified samples, with the crystalline boron consistently showing the narrowest peaks, indicative of a well-defined and less distorted crystal structure.

Table 6-3 Lattice parameters of the α/α' -titanium phase in the as-built Ti6Al4V and 0.1 wt.%B-modified Ti6Al4V alloys processed with 150W at different laser scan parameters.

Sample Type	Exposure Time	a (nm)	c (nm)	c/a ratio	a_{β} (nm)
Ti6Al4V	30 μ s	0.29212	0.46659	1.5973	
	60 μ s	0.29216	0.46671	1.5974	
	90 μ s	0.29223	0.46689	1.5977	
	120 μ s	0.29259	0.46759	1.5981	
Ti6Al4V-0.1B (Amorph)	30 μ s	0.29275	0.46649	1.5935	
	60 μ s	0.29283	0.46674	1.5939	
	90 μ s	0.29286	0.46685	1.5941	
	120 μ s	0.29353	0.46852	1.5962	0.32060
Ti6Al4V-0.1B (Cryst)	30 μ s	0.29291	0.46658	1.5929	
	60 μ s	0.29309	0.46705	1.5935	
	90 μ s	0.29315	0.46732	1.5941	
	120 μ s	0.29364	0.46842	1.5952	0.32132

From (10 $\bar{1}$ 1) peak positions in Figure 6-7(c), lattice parameters for α/α' -titanium phase of the samples were measured to distinguish the α and α' -titanium phase from XRD spectra, as shown in Table 6-3. Increasing exposure time increased the values of a, c, as well as the c/a ratio of the α/α' -titanium phase. This phenomenon can be attributed to the diffusion of solute atoms during solidification process. The metastable α' -titanium phase in the as-built specimen has a high concentration of vanadium, whose atomic radius (0.132nm) is lower than that of titanium (0.147nm) (Sallica-Leva et al., 2016). During slower cooling rates, vanadium atoms have sufficient time to diffuse significantly in the matrix, hence the lattice of α/α' -titanium phase slightly expands, causing 2θ values to shift towards low diffraction angles. From Table 6-3, it can also be concluded the α' -titanium phase had smaller ratios of c/a than more stable α -titanium phase. The β -phase lattice parameters of amorphous and crystalline boron-modified samples were also calculated as 0.3206nm and 0.32132nm, with β -phase contents of 4.5% and 4.86%, respectively.

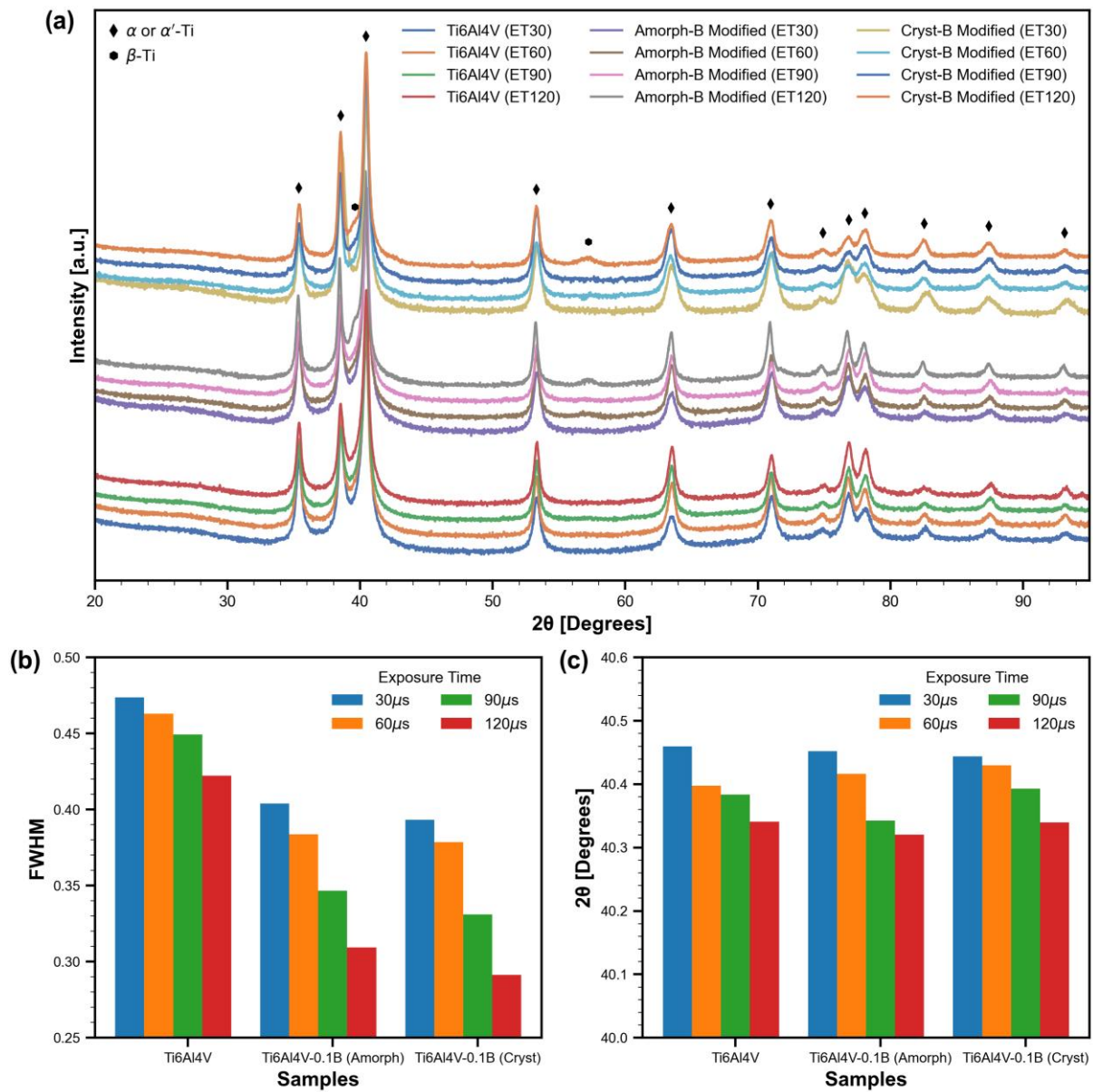


Figure 6-7 (a) XRD spectra of Ti6Al4V and 0.1 wt.%B-modified Ti6Al4V alloys processed with 150W at different laser scan parameters; (b) the evolution of full width at half maximum (FWHM) and (c) 2 θ peak position of the α/α' (10 $\bar{1}$ 1) peak across different laser scan parameters.

Figure 6-8(a) shows the XRD spectra of as-built unmodified, amorphous and crystalline boron-modified Ti6Al4V alloy samples processed at different exposure times from 120 μ s up to 450 μ s using 100W laser power, respectively. As in the case of 150W laser power, the unmodified Ti6Al4V samples exhibited only α/α' -titanium peaks across all laser scan parameters, with no detectable β -titanium peaks. These α/α' -titanium peaks were remarkably broad, yet their broadness was less compared to the 150W laser power condition. Contrary to 150W condition, the main α/α' (10 $\bar{1}$ 1) peak across different laser scan parameters showed a shift to lower 2 θ values, indicating an increase in the lattice parameter for the sample. The addition of boron

showed a noticeable narrowing of the main α/α' -titanium peak compared to unmodified alloy samples. Significant changes in phase composition were also observed as the exposure time increased. At exposure time of 120 μ s, the XRD spectra for both amorphous and crystalline boron-modified samples showed predominantly α/α' -titanium peaks, indicating the presence of the martensitic α' phase. However, as the exposure time increased to 180 μ s, tiny β -phase peaks emerged, suggesting the beginning of $\alpha' \rightarrow \alpha + \beta$ phase transformation. With further increases in exposure time, β -phase peaks became stronger. This trend indicates that longer exposure times lead to a more complete phase transformation, with the crystalline boron-modified samples exhibiting a more pronounced and rapid phase transformation compared to their amorphous counterparts. The increase in peak intensity with longer exposure times also suggests a higher volume fraction of the β -phase in these samples. Figure 6-8(b) shows the FWHM of the main α/α' peak for Ti6Al4V and 0.1 wt.% B-modified Ti6Al4V alloys processed with 100W at various laser scan parameters. In the unmodified samples, the FWHM were relatively high, similar to those observed at 150W, indicating distorted microstructure. However, as exposure time increased, the FWHM at 100W showed a more pronounced decrease than those at 150W. The addition of boron, particularly in its crystalline form, resulted in a more pronounced reduction in FWHM compared to the unmodified alloys, as was observed in the 150W case. As exposure time increased from 120 μ s to 450 μ s, both amorphous and crystalline boron-modified samples showed a continued decrease in FWHM, with the crystalline boron consistently producing the narrowest peaks.

Table 6-4 Lattice parameters of the α/α' -titanium phase in the as-built Ti6Al4V and 0.1 wt.%B-modified Ti6Al4V alloys processed with 100W at different laser scan parameters.

Sample Type	Exposure Time	a (nm)	c (nm)	c/a ratio	a_β (nm)	V_β (%)
Ti6Al4V	120 μ s	0.292230	0.465950	1.5945		
	180 μ s	0.292420	0.466677	1.5959		
	225 μ s	0.292610	0.467020	1.5960		
	300 μ s	0.292800	0.467380	1.5962		
	450 μ s	0.293090	0.467893	1.5964		
Ti6Al4V-0.1B (Amorph)	120 μ s	0.292010	0.465850	1.5953	0.32128	0
	180 μ s	0.292910	0.467580	1.5963	0.32115	3.71
	225 μ s	0.292930	0.467630	1.5964	0.32092	4.02
	300 μ s	0.292970	0.467730	1.5965	0.32060	4.33
	450 μ s	0.293360	0.468399	1.5967	0.32051	5.77
Ti6Al4V-0.1B (Cryst)	120 μ s	0.292680	0.467010	1.5956	0.32143	0
	180 μ s	0.292740	0.467290	1.5963	0.32107	4.08
	225 μ s	0.292850	0.467530	1.5965	0.32081	4.47
	300 μ s	0.292940	0.467850	1.5971	0.32058	5.39
	450 μ s	0.293219	0.468370	1.5973	0.32004	7.39

From (10 $\bar{1}$ 1) peak positions in Figure 6-8(c), lattice parameters for α/α' -titanium and β -titanium phases of the samples processed with 100W at different laser scan parameters were measured from XRD spectra, as shown in Table 6-4. The lattice parameters a, c and the c/a ratio generally

increased with increasing exposure time, similar to the trend observed in the 150W case. This increase in lattice parameters can be attributed to the diffusion of solute atoms during the solidification process, leading to the expansion of the lattice structure. In comparison to the 150W case, the lattice parameters for samples processed at 100W with same laser scan speed showed slightly lower values for both the *a* and *c* parameters, suggesting the 100W condition may result in a slightly more refined microstructure, with less expansion of the matrix. Of particular interest are the β -phase fractions in the boron-modified samples, which were calculated using Rietveld analysis. The β -phase fractions in boron-modified samples increased significantly at 100W, with amorphous boron-modified samples rising from 4.69% at 120 μ s to 6.40% at 450 μ s, and crystalline boron-modified samples from 4.88% to 7.39% over the same range. The more significant increase in β -phase in crystalline boron-modified samples indicates crystalline boron more effectively driven phase transformation at lower laser scan parameters, enhancing β -phase presence compared to the amorphous counterpart. Additionally, the lattice parameter of the β -phase decreased due to the diffusion of vanadium, which became more concentrated in the β -phase at higher exposure times. This explains why the lattice parameter of the β -phase (a_β) in the crystalline boron-modified samples is lower, reflecting the further enrichment of vanadium in the β -phase as a result of the higher exposure times and temperatures during processing.

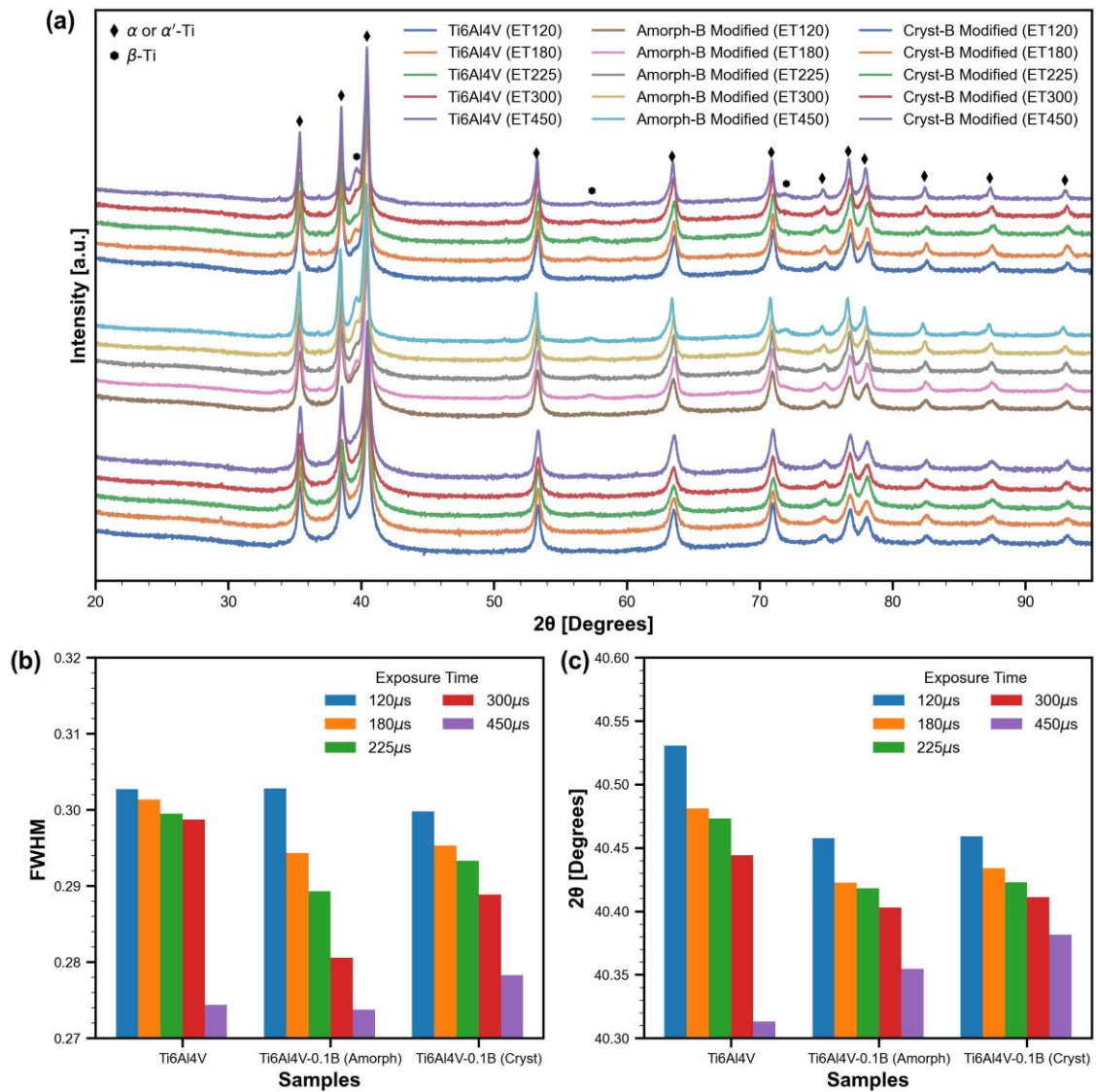


Figure 6-8 (a) XRD spectra of Ti6Al4V and 0.1 wt.%B-modified Ti6Al4V alloys processed with 100W at different laser scan parameters; (b) the evolution of full width at half maximum (FWHM) and (c) 2θ peak position of the α/α' (1011) peak across different laser scan parameters.

6.5 Microstructural Characterization

The microstructures of the bottom, middle and top layers along the build direction for unmodified Ti6Al4V samples processed at different laser exposure times are shown in Figure 6-9. At an exposure time of 30 μs , a typical acicular martensitic α' -titanium was observed in the bottom layer of the sample (Figure 6-9(a)). Similar martensitic microstructure was also seen in the middle (Figure 6-9(b)) and top (Figure 6-9(c)) layers of the sample. This observation was consistent with the rapid solidification and cooling rates expected at this shorter exposure time. This finding was further confirmed by the XRD spectra, where only α/α' peaks were detected. As the exposure time increased to 60 μs , 90 μs and 120 μs , a significant microstructural evolution

was observed. The bottom layer transformed from fully martensitic structure to $\alpha+\beta$ phase mixture (Figure 6-9(d), (g), (j)). This phase transformation can be attributed to the higher thermal input and longer cooling times in the bottom layers, promoting the stabilization of the β -titanium phase and allowing sufficient time for the α -titanium phase to form during cooling. In contrast, the middle and top layers remained dominated by typical martensitic α' -titanium phase. The rapid cooling experienced in the top layers, due to reduced heat accumulation, likely caused finer martensitic laths. This finding was further corroborated by the hardness mapping data presented in Section 6.3, showed an increase in hardness in the top region compared to the middle and bottom layers. In contrast, the middle layers, subjected to slower cooling rates, exhibited coarser martensitic structures, as reflected in their relatively lower hardness value.

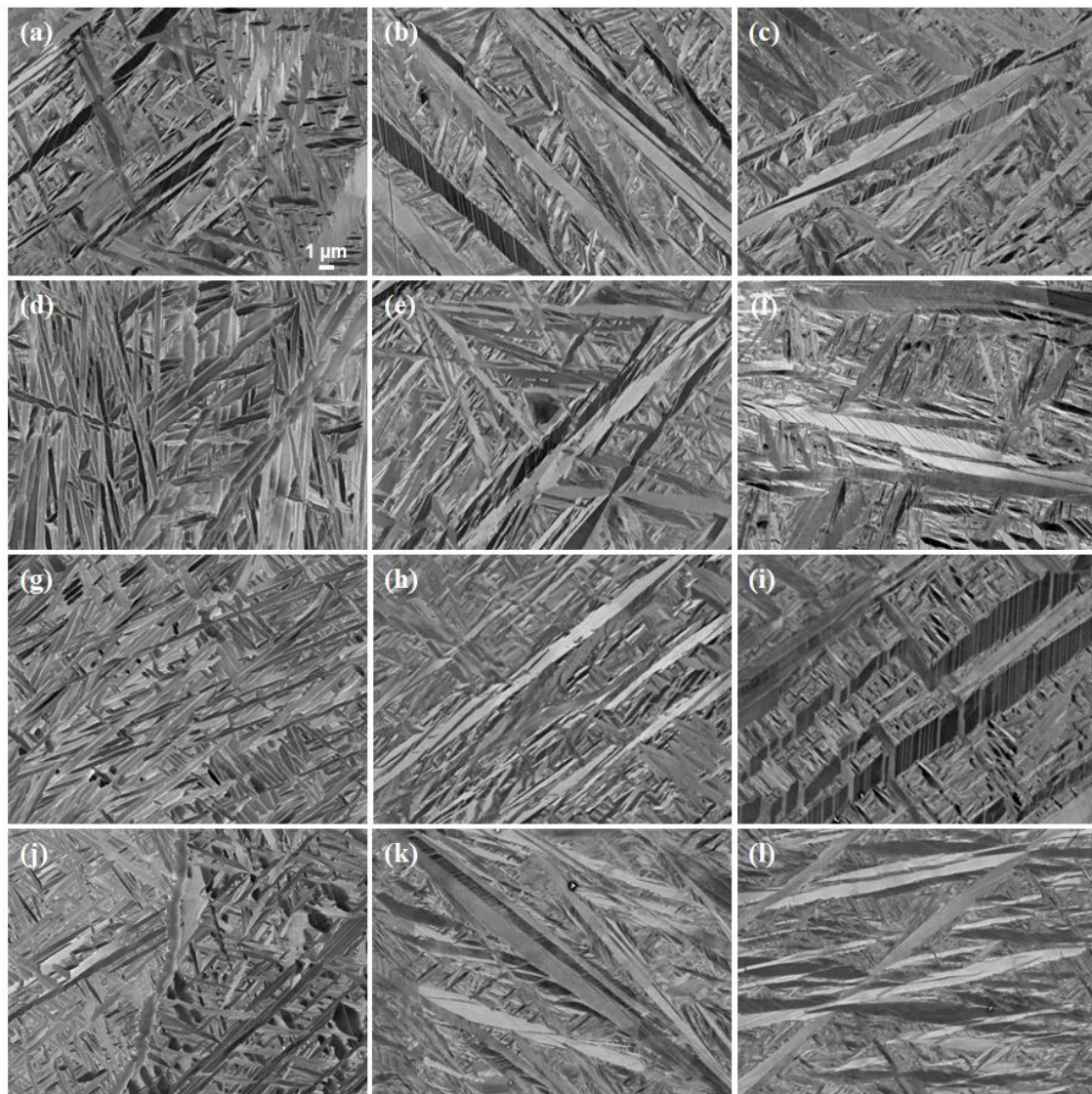


Figure 6-9 SEM-BSE images of Ti6Al4V samples produced with 150W at different laser scan parameters. Images (a), (d), (g), and (j) correspond to the bottom layer; (b), (e), (h), and (k) the middle layer, and (c), (f), (i), and (l) the top layer. The samples were processed using laser exposure times of 30 μ s, 60 μ s, 90 μ s, and 120 μ s, from top to bottom.

Figure 6-10 shows the bottom, middle and top layers along the build direction for 0.1 wt.% amorphous boron-modified Ti6Al4V samples produced at different laser scan speeds. At the shortest exposure time of 30 μ s, the bottom region exhibited a clear $\alpha+\beta$ phase, contrasting with unmodified Ti6Al4V sample. The middle and top layers, however, displayed predominantly martensite, likely due to the rapid cooling in these areas, preventing full phase transformation. As the exposure time increased to 60 μ s, the bottom region continued to display a stable $\alpha+\beta$ phase mixture, while the middle and top regions retained martensitic structures. However, the martensite in the top layer appeared finer compared to that in the middle layer. Although the microstructure in the middle section of 90 μ s was dominated by martensite and XRD failed to detect any β -titanium, the middle region showed the beginning of a phase transition in isolated locations. The bottom and top layers remained predominantly $\alpha+\beta$ and martensitic, respectively. At the longest exposure time of 120 μ s, the bottom and middle layers showed a distinct $\alpha+\beta$ phase mixture, while the top region retained a martensite. All samples, regardless of exposure time, exhibited TiB particles, with particle size likely increasing with longer exposure times. In contrast to unmodified alloy, where martensite dominated, boron-modified samples consistently displayed $\alpha+\beta$ phases in the bottom region and in the middle at the longest exposure time.

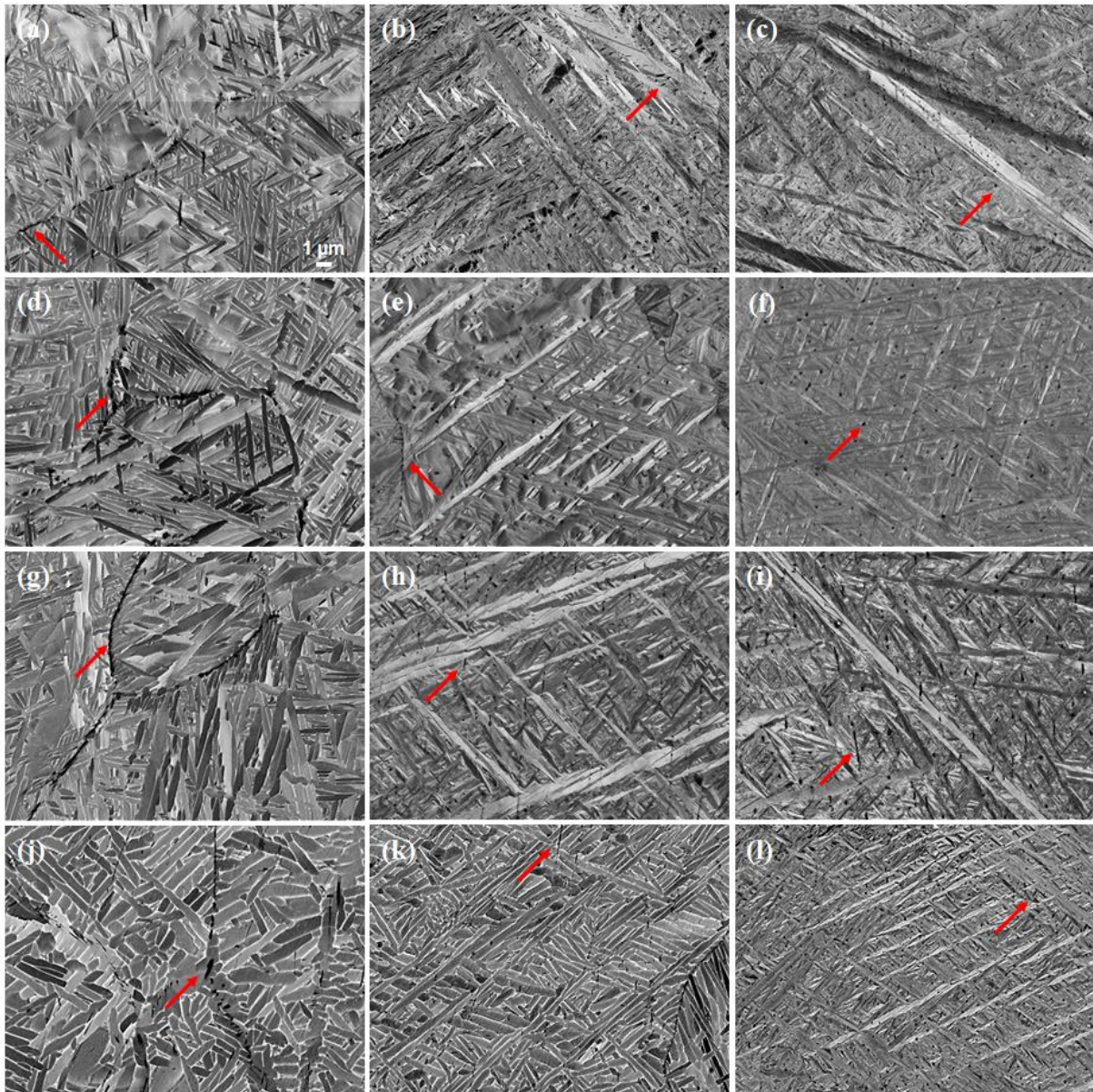


Figure 6-10 SEM-BSE images of Ti6Al4V-0.1B (Amorph) samples produced with 150W at different laser scan parameters. Images (a), (d), (g), and (j) correspond to the bottom layer; (b), (e), (h), and (k) the middle layer; and (c), (f), (i), and (l) the top layer. The samples were processed using laser exposure times of 30 μ s, 60 μ s, 90 μ s, and 120 μ s, from top to bottom. Red arrows indicate TiB particles.

Figure 6-11 shows the microstructures of the bottom, middle, and top layers along the build direction for 0.1 wt.% crystalline boron-modified Ti6Al4V samples produced at various laser scan parameters. Similar to the amorphous boron-modified samples, the bottom layers consistently exhibited a clear α + β phase mixture across all exposure times, in contrast to unmodified Ti6Al4V, where martensitic structures typically dominated the bottom layers. TiB particles, as indicated by the red arrows, were visible throughout the microstructure and appeared to increase in size with longer exposure times. The middle and top layers displayed predominantly martensitic structures at shorter exposure times, with finer martensite in the top

layers. With increasing exposure time, the middle region began to show signs of phase transformation, with possible coexistence of $\alpha+\beta$ and martensite at 90 μ s, transforming to a complete $\alpha+\beta$ at 120 μ s. The top region remained martensitic, consistent with the amorphous boron-modified samples. Overall, the microstructural evolution in crystalline boron-modified Ti6Al4V followed a similar trend to that observed in the amorphous boron-modified samples.

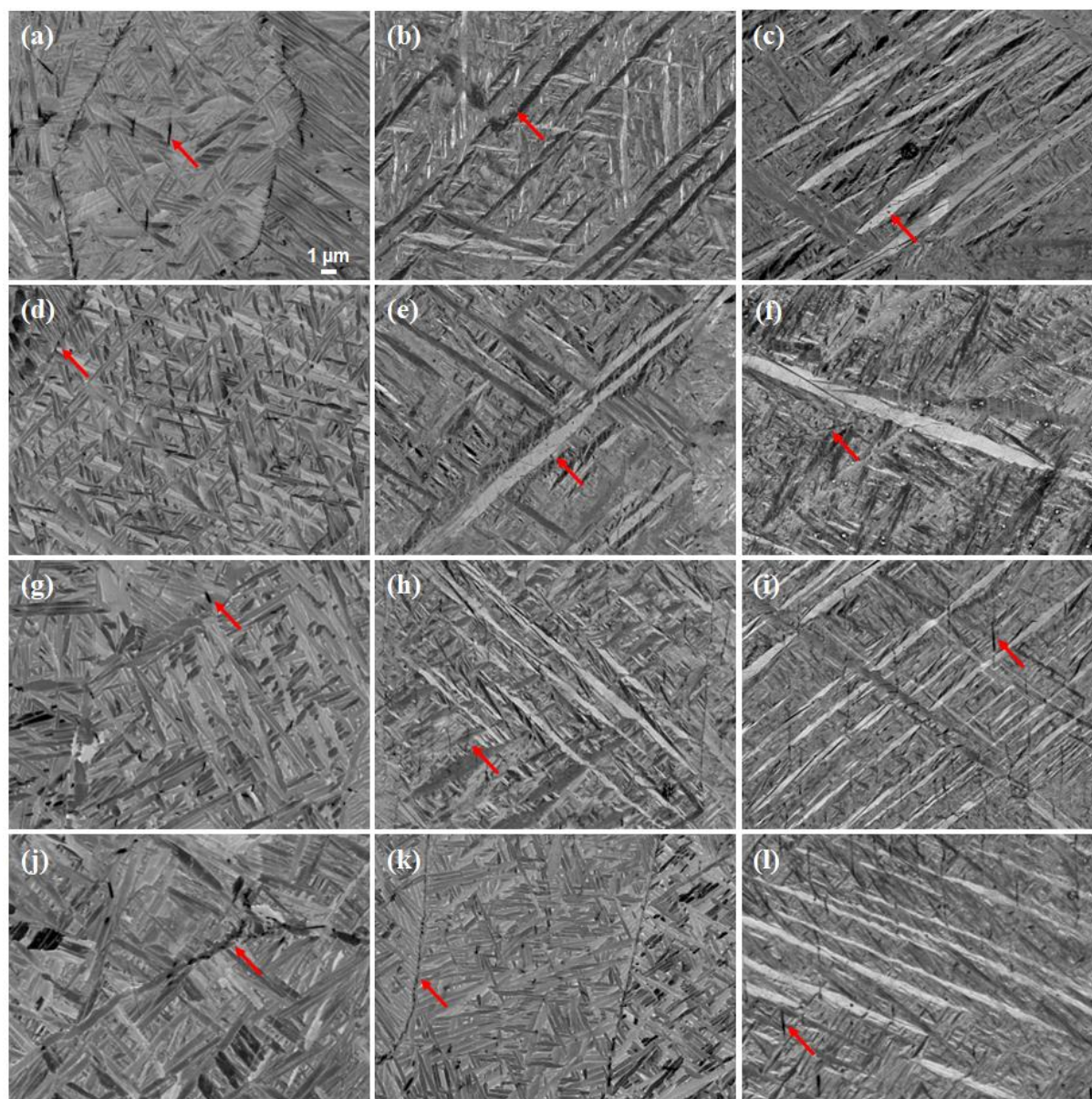


Figure 6-11 SEM-BSE images of Ti6Al4V-0.1B (Cryst) samples produced with 150W at different laser scan parameters. Images (a), (d), (g), and (j) correspond to the bottom layer; (b), (e), (h), and (k) the middle layer; and (c), (f), (i), and (l) the top layer. The samples were processed using laser exposure times of 30 μ s, 60 μ s, 90 μ s, and 120 μ s, from top to bottom. Red arrows indicate TiB particles.

Figure 6-12 shows the SEM-BSE images of the middle layers of unmodified and 0.1 wt.%B-modified Ti6Al4V alloys processed with 100W at varying laser scan parameters. At the shortest

exposure time of 120 μ s, α' -titanium was observed across all samples—unmodified (Figure 6 12(a)), amorphous (Figure 6 12(a')), and crystalline boron-modified (Figure 6 12(a'')) — indicating that rapid cooling at this exposure time prevents significant phase transformation. The presence of TiB particles in the boron-modified samples was visible. As the exposure time increases to 180 μ s (Figure 6-12(b)), the unmodified alloy still showed martensitic α' -titanium, while the amorphous boron-modified sample (Figure 6-12(b')) demonstrated $\alpha+\beta$ phase mixture. The crystalline boron-modified alloy (Figure 6-12(b'')) showed a more refined $\alpha+\beta$ phase presence and larger TiB particles. At 225 μ s (Figure 6-12(c)), the same pattern continued such that unmodified Ti6Al4V retained a martensitic structure, while both boron-modified samples showed more distinct $\alpha+\beta$ phase formation, with TiB particles growing in size, especially in the crystalline boron-modified sample (Figure 6-12(c'')). At longer exposure times of 300 μ s (Figure 6-12(d)) and 450 μ s (Figure 6-12(e)), unmodified Ti6Al4V maintained its martensitic structure, while the $\alpha+\beta$ phase became increasingly prominent in both boron-modified alloys. The TiB particles, indicated by red arrows, also appeared to grow with increasing exposure time. This trend was more pronounced in the crystalline boron-modified samples (Figure 6-12(d'') and (e'')), where the particle size was larger compared to the amorphous-modified samples (Figure 6-12(d') and (e')). The boron-modified samples showed consistent $\alpha+\beta$ phase formation and TiB particle presence at all exposure times, highlighting the role of boron in stabilizing the $\alpha+\beta$ phases and promoting TiB particle growth, especially as exposure time increases. The microstructures in the bottom and top layers were consistent with those observed in the 150W case and are therefore not included in this section.

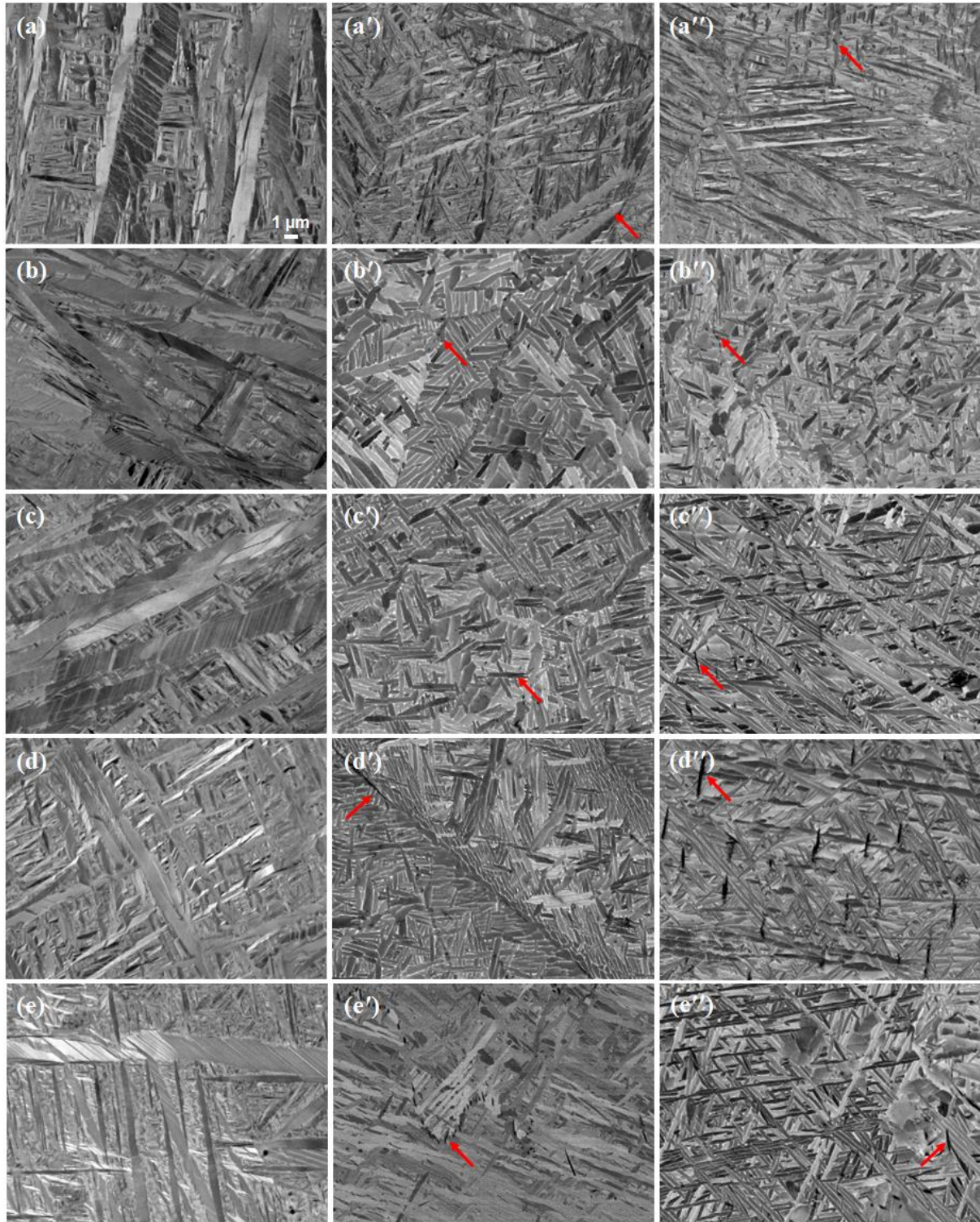


Figure 6-12 SEM-BSE images of unmodified and 0.1 wt.%B-modified Ti6Al4V alloys processed with 100W at different laser scan parameters. Images (a) to (e) represent middle layers along the build direction for Ti6Al4V processed at ET120, ET180, ET225, ET300, and ET450, respectively. Images (a') to (e') depict the corresponding microstructures for amorphous boron-modified alloys, and (a'') to (e'') for crystalline boron-modified alloys under the same conditions. Red arrows indicate TiB particles.

The development of lamellar α/β and martensitic α' structures was further examined by analysing the initial few layers deposited in samples produced with extended exposure times. The support structure of the printed cube is depicted in Figure 6-13(a), showing unfused particles between the 3mm-tall supports. Following the deposition of a single layer, approximately 30 μm thick, the microstructures from area A, located on top of the unfused powder, and area B on top of the support structures are presented in Figure 6-13(b)–(d) for a sample produced using 150W at a longer exposure time. The α/β lamellae are predominant in area A, while acicular α' plates are found in area B. The same observations were made in a single-layered sample produced using boron-modified alloy. The α -lamella widths were measured using the mean intercept method, with unmodified alloy showing a width of $351\pm30\text{nm}$, while the amorphous boron-modified and crystalline boron-modified Ti6Al4V exhibited reduced widths of approximately $285\pm27\text{nm}$ and $265\pm15\text{nm}$, respectively.

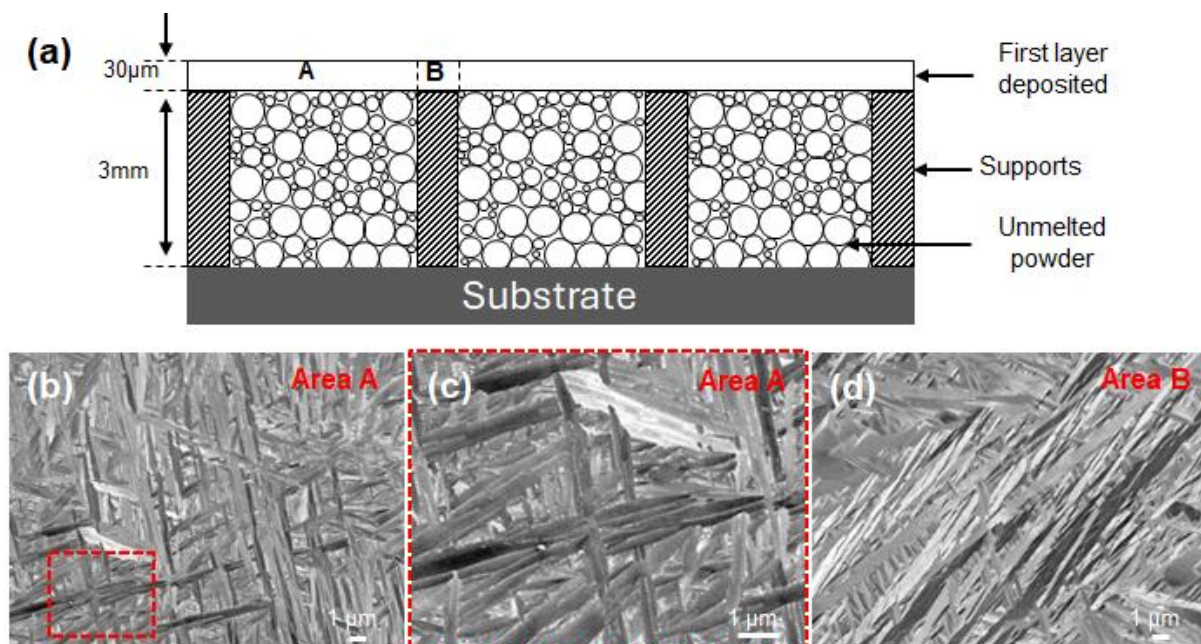


Figure 6-13 (a) Schematic representation of the build, showing the first deposited layer of Ti6Al4V ($\sim 30\text{ }\mu\text{m}$ thick) on top of a 3mm tall support structure with unmelted powder in between. (b) and (c) Microstructure of area A, located on top of the unmelted powder, revealing dominant lamellar α/β structures. (d) Microstructure of area B, located on top of the solid support, showing acicular α' plates.

After deposition of the second layer, the microstructures of the double-layered sample were analysed in both the first and second layers, specifically in regions A and B of the first layer and A' and B' of the second layer, as illustrated in Figure 6-14. In region B of the first layer, located above the support, the initially martensitic α' structure observed in the single-layered sample (Figure 6-13(d)) transformed into a lamellar α/β structure after the second layer was deposited (Figure 6-14(d)). However, in the newly deposited second layer, region B' retained a martensitic α' structure (Fig. 4d). In contrast, regions A and A', situated on top of the unfused powder,

consistently exhibited lamellar α/β microstructures in both the first and second layers (Figure 6-14(a) and (c)).

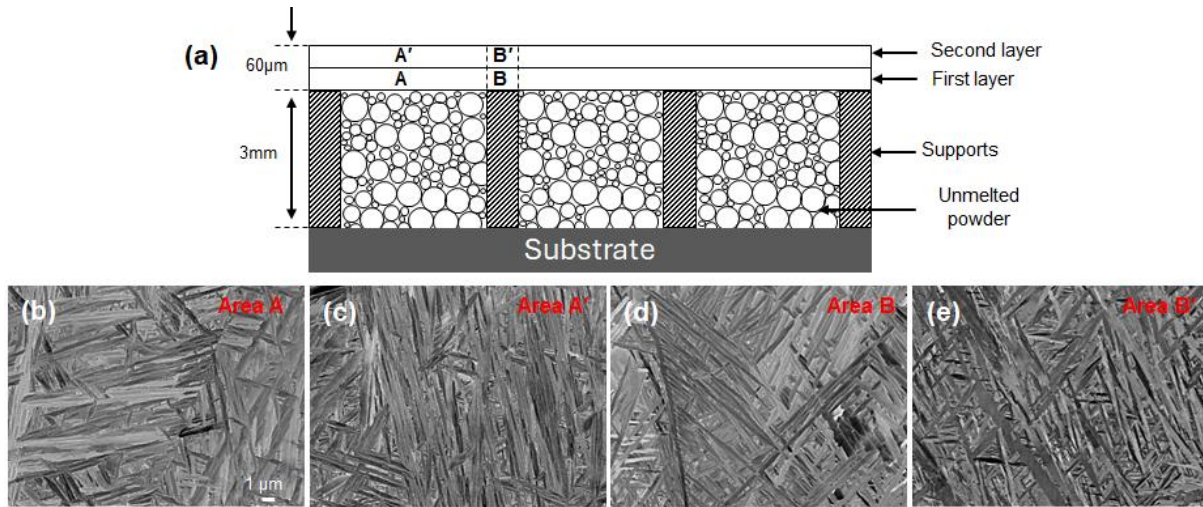


Figure 6-14 (a) Schematic representation of the build, showing the first and second deposited layers on a 3mm tall support structure with unmelted powder in between. (b) and (d) Microstructures of region A and B in the first layer, revealing lamellar α/β . (c) and (e) Microstructures of region A' and B' in the second layer, showing lamellar α/β in region A' and acicular α' plates in region B'.

In the boron-modified Ti6Al4V alloy, the microstructures after deposition of the second layer displayed similar transformations to those seen in the unmodified alloy. As shown in Figure 6-15(c) for the amorphous boron-modified sample and Figure 6-15(c') for the crystalline boron-modified sample, the martensitic α' structure present in region B (on top of the support) in the first layer transformed into a lamellar α/β structure after the deposition of the second layer. The newly deposited second layer in region B' exhibited a finer martensitic α' structure, as seen in Figure 6-15(d) for amorphous boron and Figure 6-15(d') for crystalline boron. In regions A and A' (on top of the unfused powder), lamellar α/β structures were observed in both the first and second layers, shown in Figure 6-15(a) and (b) for the amorphous boron sample and Figure 6-15(a') and (b') for the crystalline boron sample. The α -lamella width in the boron-modified alloy was noticeably finer compared to the unmodified Ti6Al4V, with a reduction in width observed across both amorphous and crystalline boron-modified variants.

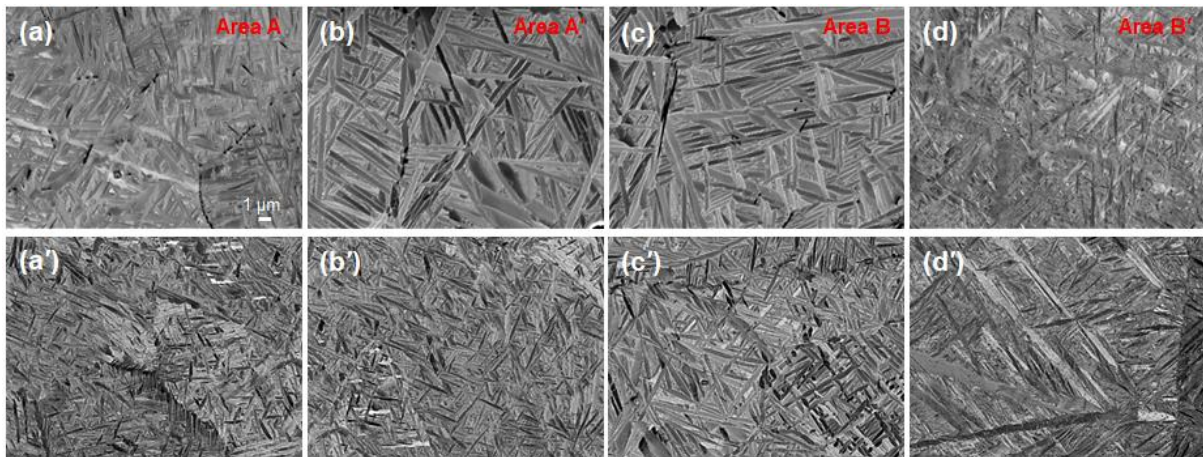


Figure 6-15 SEM-BSE images showing the microstructures in amorphous and crystalline boron-modified Ti6Al4V alloys after deposition of the second layer. (a) to (d) correspond to the amorphous boron-modified alloy, and (a') to (d') correspond to the crystalline boron-modified alloy.

Figure 6-16 shows the microstructures in regions A, B, and C from the top region of a 5mm thick deposit, where acicular α' is predominant as seen from the Figure 6-16(b) – (c). In the middle and bottom regions D and E, respectively, the microstructures varied based on the addition of boron. For the base alloy, the bottom region exhibited lamellar α/β , while the middle region remained martensitic α' phase. In contrast, the boron-modified alloys showed a distinct transformation, with lamellar α/β structures present in both the middle and bottom regions starting from a 120 μ s exposure time. This demonstrates that the boron modification promoted earlier phase transformation into α/β compared to the unmodified Ti6Al4V alloy.

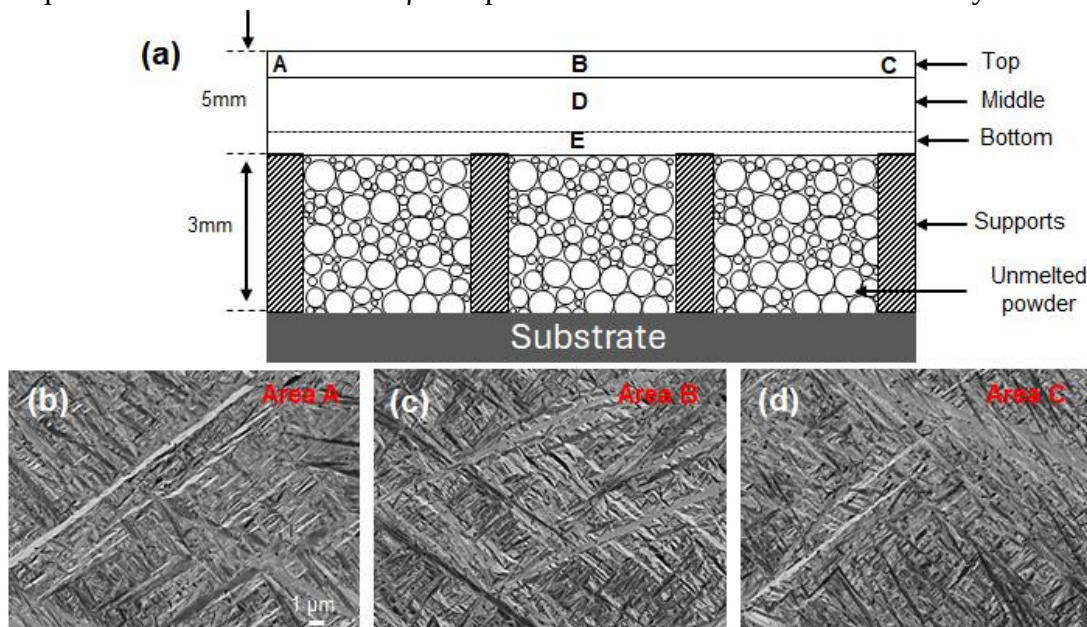


Figure 6-16 (a) Schematic representation of the build, showing the first and second deposited layers on a 3mm tall support structure with unmelted powder in between. SEM-BSE images showing (b) region A; (c) region B and (d) region C.

6.6 Size and Variant Selection of α Laths

The EBSD inverse pole figure orientation maps shown in Figure 6-17 reveal the crystallographic orientation of the α -phase across unmodified and 0.1 wt.%B-modified Ti6Al4V alloy compositions along the build direction. The pole figures depict the microstructure produced using a laser power of 150W at two distinct exposure times, 30 μ s and 120 μ s. Notably, these maps provide critical insights into the α -phase texture and its evolution as a function of processing parameters. In the case of unmodified alloy, a significant increase in α -phase width was observed with increasing exposure time, as demonstrated by the progression from 5.51 μ m at 30 μ s to 8.39 μ m at 120 μ s. This consistent growth in α -phase width indicates a direct relationship between exposure time and α -phase coarsening in the base alloy due to cooling rate. For the boron-modified Ti6Al4V alloys, different trends were observed. The amorphous boron-modified sample exhibited a lower initial α -phase width of 4.09 μ m at 30 μ s, increasing to 6.78 μ m at 120 μ s. Similarly, the crystalline boron-modified sample showed an α -phase width of 4.52 μ m at 30 μ s, reaching 6.07 μ m at 120 μ s. Although the general trend of increasing width with exposure time was maintained, the boron-modified samples exhibited slower coarsening compared to the unmodified alloy, suggesting that the addition of boron—whether in amorphous or crystalline form—induces grain refinement and inhibits α -phase growth to some extent. The crystalline boron-modified alloy showed the least increase in width, further emphasizing the grain refinement effect due to the crystalline boron particles, which act as potent nucleation sites and restrict grain growth.

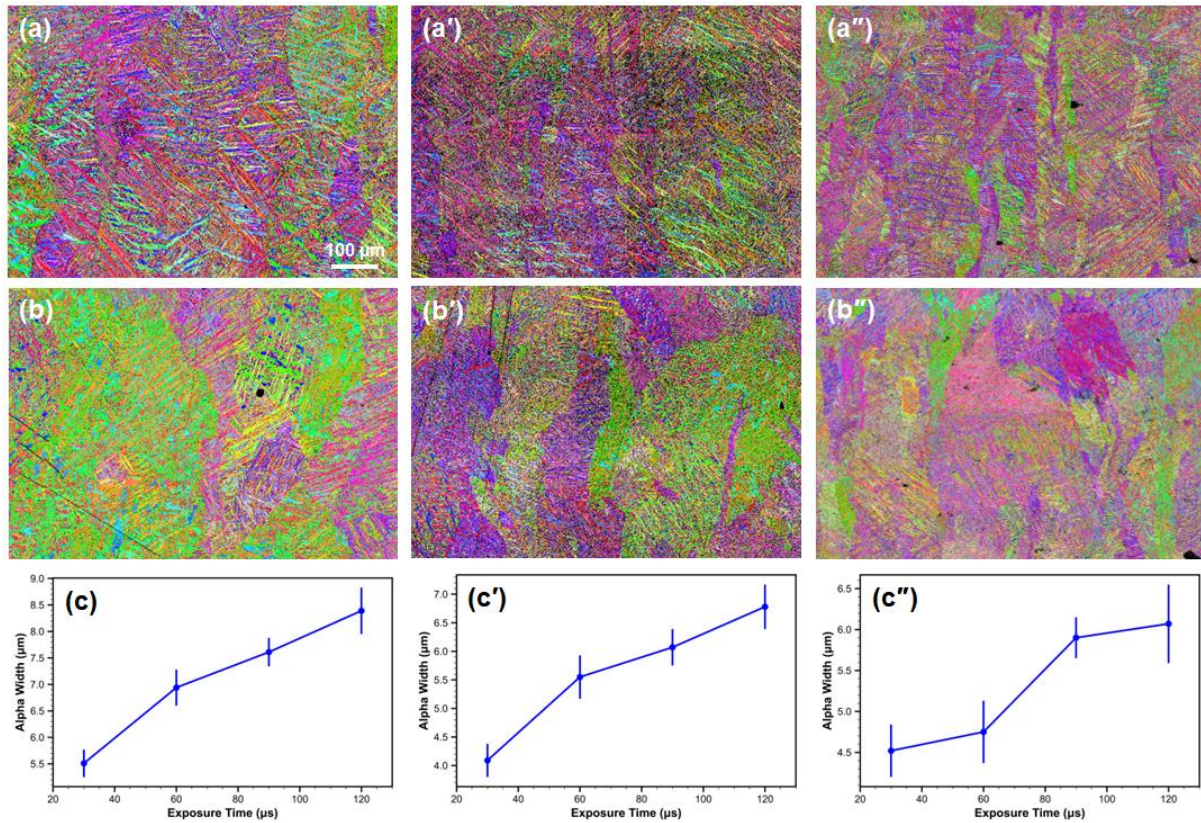


Figure 6-17 EBSD inverse pole figure orientation maps of the α , alongside the variation in α -phase width as a function of exposure time for (a) – (c) Ti6Al4V; (a') – (c') Ti6Al4V-0.1B (Amorph); (a'') – (c'') Ti6Al4V-0.1B (Cryst). The pole figures represent samples produced with a laser power of 150W at exposure times of 30 μ s and 120 μ s, respectively, for all alloy systems.

Based on the classification of α -phase variants and the methodology presented in reference (S. C. Wang et al., 2003), the 12 potential α -phase variants that can form within a prior β grain during the $\beta \rightarrow \alpha$ transformation are labelled as A, B, C, D, E, F, G, H, I, J, K, and L (Burgers, 1934; S. C. Wang et al., 2003). Among these variants, five distinct types of α/α variant boundaries can arise. Notably, Type 1 α/α variant boundaries, which occur between α -variants with identical crystallographic orientations, are excluded from further quantitative analysis due to their lack of distinguishing features. A systematic analysis was conducted on the misorientation angles (limited to those greater than 5°) between neighbouring α -variants, as displayed in Figure 6-17. To maintain statistical reliability, over 10^5 α -variants or α -laths were examined within each grain structure. The findings are presented in Figure 6-18. The distribution of the α -variant misorientation angles in the alloys processed with exposure time of 30 μ s was similar (Figure 6-18(a) – (a'')), where the Type 4 α/α boundary with a characteristic misorientation angle of $\sim 63^\circ$ was prevalent. The figure illustrates that the addition of boron, in both amorphous and crystalline forms, resulted in a broader distribution of peaks around 10° (Type 6) and 90° (Type 5). Moreover, misorientation angles between $20^\circ - 58^\circ$ and $65^\circ - 88^\circ$ were observed, which can be linked to the heterogeneous nucleation of α -phase on TiB particles. With boron inclusion, there was also a noticeable reduction in the frequency of Type

2 variant boundaries, while the frequencies of Type 5 and Type 6 variant boundaries increased. The distribution of α -variant misorientation angles in the grain-refined Ti6Al4V alloys produced at 120 μ s was similar (Figure 6-18(b) – (b'')), but the Type 3 α/α boundary, characterized by a misorientation angle of approximately 60°, became the most prevalent.

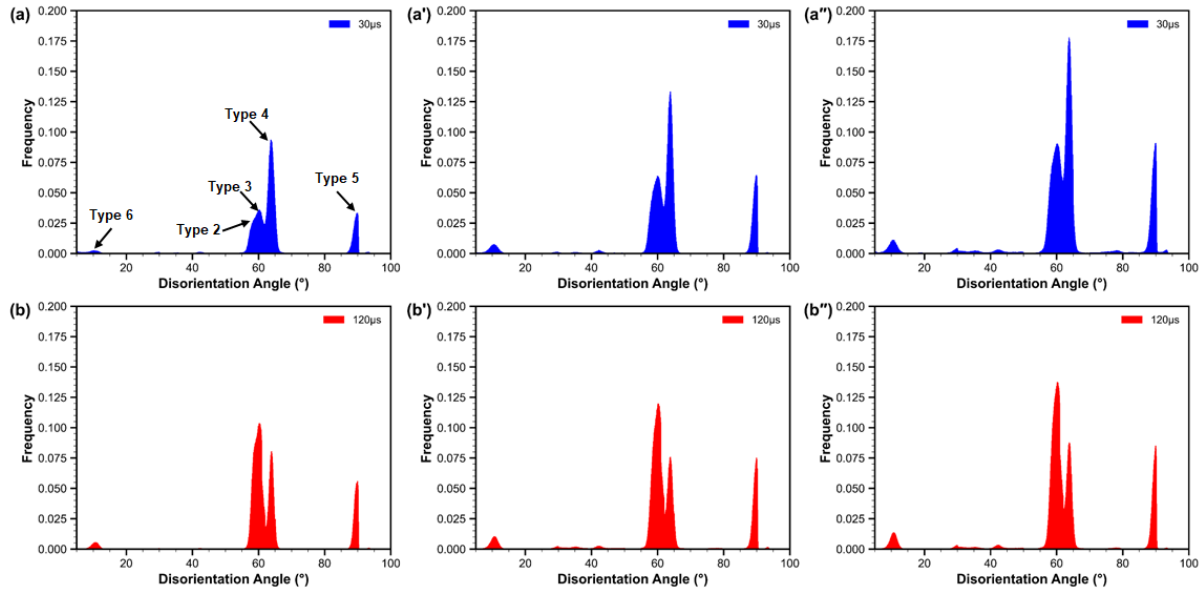


Figure 6-18 Statistical distribution of neighbouring α -variant misorientation angles for Ti6Al4V and boron-modified Ti6Al4V alloys processed by PBF-LB/M with 150W. (a) shows the distribution for Ti6Al4V processed with 30 μ s, (a') and (a'') represent the amorphous and crystalline boron-modified alloy processed under the same condition, respectively. (b) presents the distribution for Ti6Al4V processed with 120 μ s, with (b') and (b'') showing the amorphous and crystalline boron-modified alloy under identical conditions. Distinct variant types (Types 2-6) are labelled in (a), highlighting frequent misorientation angles observed for different α -variants.

6.7 Reconstructed Prior- β Microstructure and Texture

Parent β -grain reconstruction process was carried out based on OM image and the EBSD results obtained from unmodified and 0.1 wt.%B-modified Ti6Al4V alloy compositions on the XZ surface. The EBSD inverse pole figure orientation maps of the reconstructed prior- β grains for samples processed with 150W at different laser scan speeds is shown in Figure 6-19. At exposure time of 30 μ s, the reconstructed β grains of the unmodified Ti6Al4V alloy (Figure 6-19(a)) showed a highly columnar β -titanium phase microstructure with elongated grains, indicating strong texture and minimal grain misorientation. The incorporation of amorphous boron (Figure 6-19(a')) seemed to introduce more grain refinement and diversity in grain orientation. While the columnar structure persisted, the grains appeared somewhat smaller. Compared to the amorphous boron variant, the crystalline boron-modified alloy (Figure 6-19(a'')) showed a more disrupted columnar structure with a higher level of grain orientation variations. Similar to 30 μ s, the β -titanium grains remained highly columnar and elongated, although some grain refinement was observed in 60 μ s case for unmodified alloy samples

(Figure 6-19(b)). In the amorphous boron-modified alloy (Figure 6-19(b')), significant grain refinement was visible. The columnar nature was retained, but with more frequent grain boundary interactions and misorientation. The crystalline boron-modified variant (Figure 6-19(b'')) showed a marked grain refinement and increased grain misorientation compared to the amorphous boron-modified case, suggesting weaker crystallographic texture. At 90 μ s, the grain refinement continued for unmodified alloy sample (Figure 6-19(c)). The columnar structure was still prominent, but the β grains were finer than at 60 μ s. This indicates that the longer exposure time had a refining effect on grain size and texture. In amorphous boron-modified case (Figure 6-19(c')), the prior-grains were further refined, and the microstructure showed a high degree of misorientation, indicating potential dynamic recrystallization effects. The crystalline boron-modified alloy (Figure 6-19(c'')) showed even more grain refinement and significant misorientation though some relatively big columnar prior-grains were visible. The columnar structure was mainly disrupted, with smaller and more equiaxed grains becoming visible. Further increasing the exposure time to 120 μ s caused prior- β grains becoming notably finer compared to the previous exposure times for unmodified alloy (Figure 6-19(d)). The columnar β -grains was disrupted and appeared more equiaxed, reflecting a stronger grain refinement mechanism possibly linked to the prolonged laser exposure. The refinement of prior- β grains continued with amorphous boron addition (Figure 6-19(d')), with more equiaxed and finer grains. The grain refinement was also significant, with a fully disrupted columnar structure for crystalline boron-modified alloy (Figure 6-19(d'')). Grains were small and equiaxed, with more noticeable grain boundary misorientations.

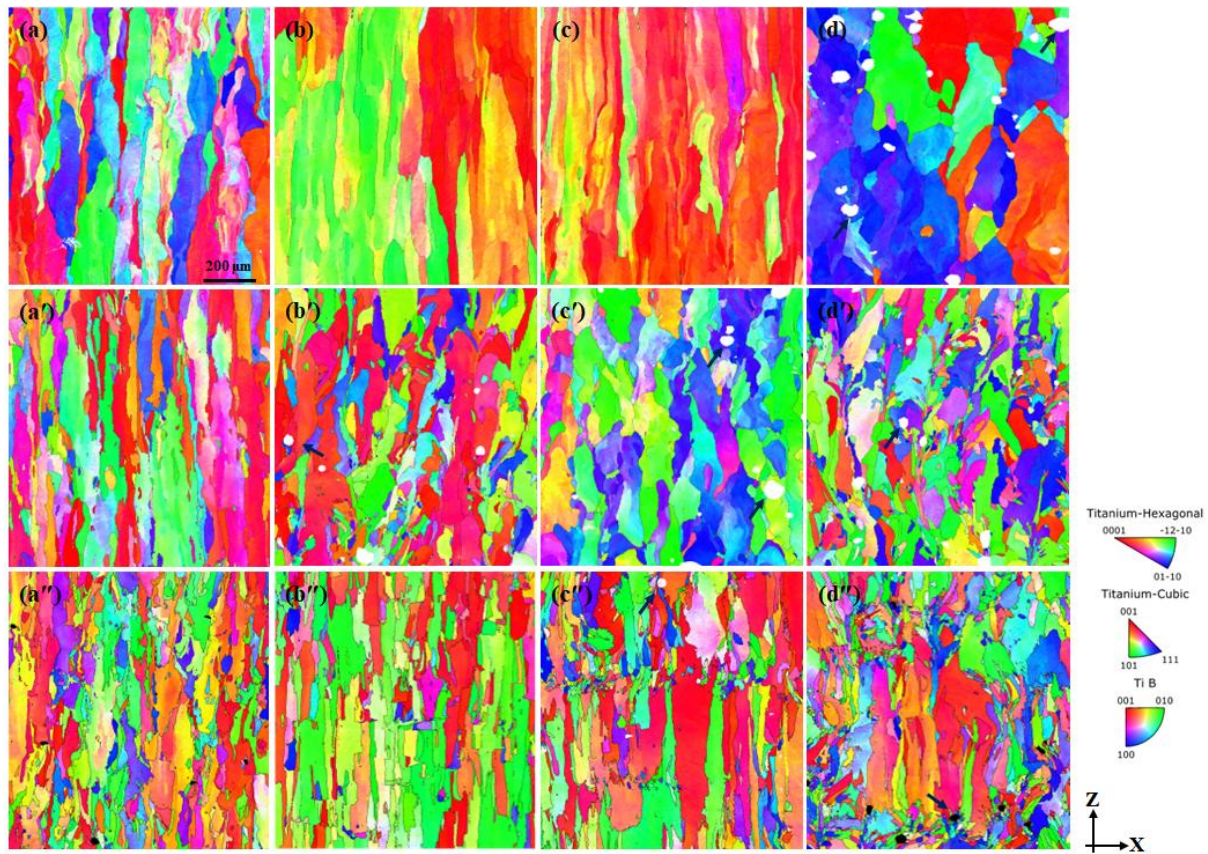


Figure 6-19 EBSD inverse pole figure orientation maps of reconstructed β phase of Ti6Al4V and 0.1 wt.%B-modified Ti6Al4V alloys processed with 150W at different laser scan parameters. Images (a) to (d) represent Ti6Al4V alloy processed with exposure times ET30, ET60, ET90, and ET120, respectively. Images (a') to (d') show the corresponding map for the alloy modified with amorphous boron under the same exposure conditions, while images (a'') to (d'') illustrate the maps for the alloy modified with crystalline boron under identical exposure parameters. The black arrows indicate pores found in the region of interest.

Table 6-5 provides the reconstructed prior- β grain dimensions (major and minor axes) and aspect ratios for Ti6Al4V and 0.1 wt.% B-modified Ti6Al4V alloys processed with 150W at various exposure times. A grain is classified as equiaxed when its aspect ratio is less than 3, while columnar grains have aspect ratios of 3 or higher (Biscuola & Martorano, 2008; K. V. Yang et al., 2018). According to this classification, unmodified alloy exhibited predominantly columnar grains across all exposure times, with aspect ratios ranging from 4.88 at 30 μ s to 3.76 at 120 μ s. The grain dimensions decrease with increasing exposure time, as the major axis shrinks from 115.38 μ m at 30 μ s to 95.1 μ m at 120 μ s, and the minor axis similarly decreases from 23.65 μ m to 25.26 μ m. This indicates that while the grain structure remains columnar, grain refinement occurs with longer exposure times. In the Ti6Al4V-0.1B (amorphous) alloy, there was significant grain refinement as well. The aspect ratio decreased from 5.08 at 30 μ s to 2.37 at 120 μ s, showing a clear transition from columnar to more equiaxed grains. This refinement was accompanied by a substantial reduction in both the major and minor axes, with the major

axis reducing from 66.18 μm to 24.42 μm and the minor axis decreasing from 13.02 μm to 10.32 μm . The Ti6Al4V-0.1B (crystalline) alloy showed the most significant grain refinement and aspect ratio reduction. The aspect ratio decreased from 4.47 at 30 μs to 2.65 at 120 μs , suggesting a transition toward more equiaxed grains at longer exposure times. The major axis shrank drastically from 59.88 μm at 30 μs to 32.23 μm at 120 μs , while the minor axis follows a similar trend, reducing from 13.41 μm to 12.18 μm . This indicates a substantial grain refinement, with grains becoming more equiaxed over time.

Table 6-5 Reconstructed prior- β grain dimensions of Ti6Al4V and 0.1 wt.%B-modified Ti6Al4V alloys processed with 150W at different laser scan parameters.

Sample Type	Exposure Time	Fitted Ellipse Major Axis (μm)	Fitted Ellipse Minor Axis (μm)	Aspect Ratio
Ti6Al4V	30 μs	115.38	23.65	4.88
	60 μs	113.87	28.49	4.00
	90 μs	99.6	24.95	3.99
	120 μs	95.1	25.26	3.76
Ti6Al4V-0.1B (Amorph)	30 μs	66.18	13.02	5.08
	60 μs	55.83	15.15	3.69
	90 μs	56.45	14.50	3.89
	120 μs	24.42	10.32	2.37
Ti6Al4V-0.1B (Cryst)	30 μs	59.88	13.41	4.47
	60 μs	46.37	14.81	3.13
	90 μs	41.48	15.27	2.72
	120 μs	32.23	12.18	2.65

The EBSD inverse pole figure orientation maps of the reconstructed β phase of unmodified and boron-modified Ti6Al4V alloys processed with 100W at various exposure times shown in Figure 6-20 offer distinct observations with respect to in-situ grain refinement. At exposure time of 120 μs , the Ti6Al4V alloy (Figure 6-20(a)) displayed a predominantly disrupted columnar grain structure with elongated β grains. The microstructure was relatively coarse, with visible large grains. The introduction of amorphous boron (Figure 6-20(a')) lead to noticeable grain refinement, resulting in a finer prior- β structure compared to the unmodified alloy. In the crystalline boron-modified sample (Figure 6-20(a'')), the grain refinement was more significant, with further disruption in the columnar texture. Grains were smaller and more misoriented. At 180 μs , the grain structure of the unmodified Ti6Al4V (Figure 6-20(b)) showed a relatively smaller columnar prior grains and likely less texture compared to 120 μs , but the grains were still relatively large. The addition of amorphous boron (Figure 6-20(b')) resulted in further grain refinement. The columnar structure persisted, but the grains were smaller and more equiaxed compared to the unmodified sample. The crystalline boron-modified sample (Figure 6-20(b'')) showed the highest degree of grain refinement. The columnar structure was almost entirely disrupted, with finer grains and more grain misorientation. By increasing the exposure time to 225 μs , the Ti6Al4V alloy (Figure 6-20(c)) showed more pronounced grain refinement, with

finer columnar grains than in the previous exposure times. However, the long columnar structure was still retained. The amorphous boron-modified alloy (Figure 6-20(c')) continued to display grain refinement, with a smaller and more equiaxed grain structure compared to 180 μ s. The crystalline boron-modified sample (Figure 6-20(c'')) showed the most significant grain refinement and grain boundary misorientation. The grain structure was almost entirely equiaxed, with finer grains and higher disruption in the columnar texture.

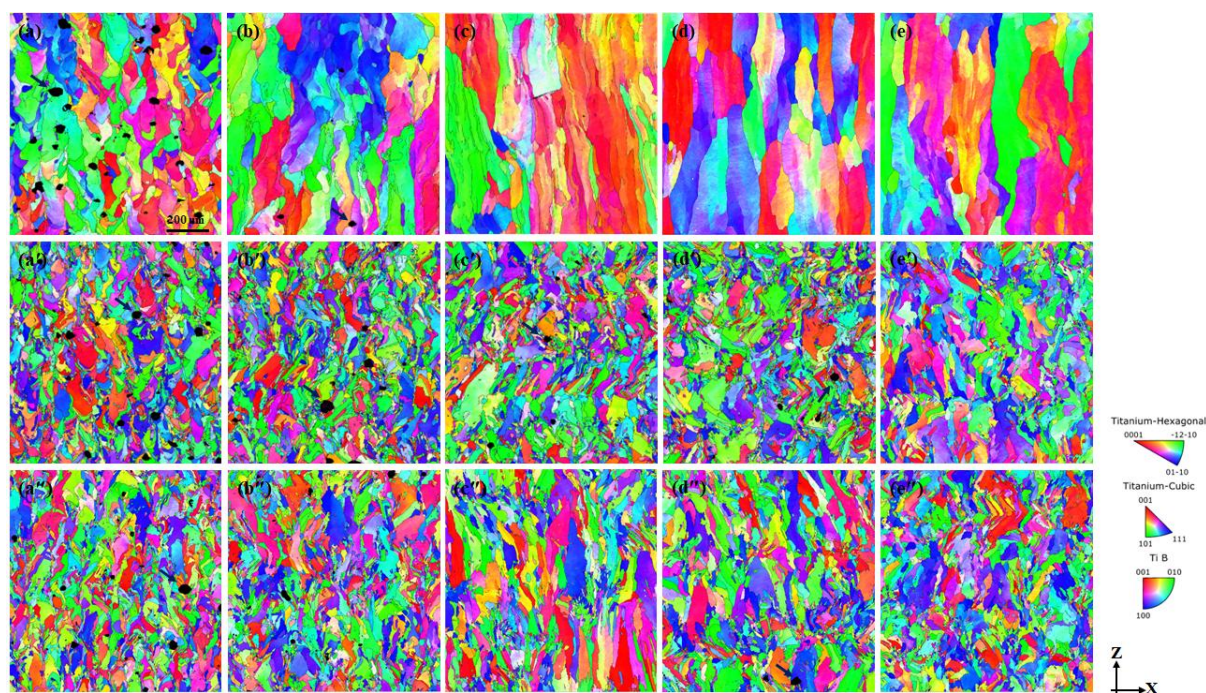


Figure 6-20 EBSD inverse pole figure orientation maps of reconstructed β phase of Ti6Al4V and 0.1 wt.%B-modified Ti6Al4V alloys processed with 100W at different laser scan parameters. Images (a) to (d) represent Ti6Al4V alloy processed with exposure times ET120, ET180, ET225, ET300 and ET450, respectively. Images (a') to (d') show the corresponding map for the alloy modified with amorphous boron under the same exposure conditions, while images (a'') to (d'') illustrate the maps for the alloy modified with crystalline boron under identical exposure parameters. The black arrows indicate pores found in the region of interest.

At 300 μ s, the grains in the Ti6Al4V alloy became significantly finer, but the columnar structure persisted as seen in Figure 6-20(d). The amorphous boron-modified alloy (Figure 6-20(d')) showed continued grain refinement, with finer and more equiaxed grains than at 225 μ s. The crystalline boron-modified sample in Figure 6-20(d'') exhibited even finer grains, with a largely equiaxed structure with higher degree of grain misorientation. At the highest exposure time, 450 μ s, the Ti6Al4V alloy (Figure 6-20(e)) showed the finest grains yet, but the columnar grain structure was still observable, although much refined. The amorphous boron-modified sample showed a fully equiaxed grain structure with significant grain refinement as seen in Figure 6-20(e'). The crystalline boron-modified alloy (Figure 6-20(e'')) displayed the highest degree of grain refinement and misorientation, with almost a fully equiaxed structure.

Table 6-6 provides reconstructed prior- β grain dimensions (major and minor axes) and aspect ratios for unmodified and 0.1 wt.% B-modified Ti6Al4V alloys processed with 100W at various exposure times. For the unmodified alloy, the aspect ratio remained above 3 across all exposure times, indicating that the grains retained a columnar structure. The grain size increased with exposure time, as seen in the growth of the major axis from 68.87 μm at 120 μs to 255.02 μm at 450 μs . Similarly, the minor axis increased from 21.42 μm to 48.24 μm over the same period, reflecting overall grain growth with longer exposure times. The aspect ratio ranged from 3.22 to 5.30, showing that the columnar nature of the grains became more pronounced at higher exposure times. In the Ti6Al4V-0.1B (amorphous) alloy, the aspect ratios generally decreased with increasing exposure time, indicating a transition from columnar to more equiaxed grains. The major axis decreased from 29.17 μm at 120 μs to 22.41 μm at 450 μs , while the minor axis decreased slightly from 12.20 μm to 10.52 μm . The aspect ratio dropped from 2.39 to 2.13, signifying that this alloy experienced significant grain refinement and began to adopt a more equiaxed structure at higher exposure times. The Ti6Al4V-0.1B (crystalline) alloy showed the most significant grain refinement, with the major axis shrinking from 25.48 μm at 120 μs to 16.93 μm at 450 μs . The minor axis remained relatively consistent, ranging from 8.66 μm to 8.63 μm . The aspect ratio decreased from 2.94 at 120 μs to 1.96 at 450 μs , indicating a clear shift from columnar to equiaxed grains. This result suggests that the crystalline boron modification was particularly effective in promoting equiaxed grain formation as exposure time increases.

Table 6-6 Reconstructed prior- β grain dimensions of Ti6Al4V and 0.1 wt.%B-modified Ti6Al4V alloys processed with 100W at different laser scan parameters.

Sample Type	Exposure Time	Fitted Ellipse Major Axis (μm)	Fitted Ellipse Minor Axis (μm)	Aspect Ratio
Ti6Al4V	120 μs	68.87	21.42	3.22
	180 μs	139.54	42.01	3.32
	225 μs	169.10	48.54	3.48
	300 μs	202.86	65.32	3.90
	450 μs	255.02	48.12	5.30
Ti6Al4V-0.1B (Amorph)	120 μs	29.17	12.20	2.39
	180 μs	26.53	11.29	2.35
	225 μs	24.33	10.51	2.31
	300 μs	23.38	10.28	2.27
	450 μs	22.41	10.52	2.13
Ti6Al4V-0.1B (Cryst)	120 μs	25.48	8.66	2.94
	180 μs	21.11	7.29	2.90
	225 μs	18.19	7.73	2.35
	300 μs	17.86	8.53	2.09
	450 μs	16.93	8.63	1.96

The pole figures of reconstructed β -grains presented in Figure 6-21 provide a clear indication of the texture evolution in Ti6Al4V and 0.1 wt.% B-modified Ti6Al4V alloys processed with 150W at various laser exposure times. The texture index values, which quantify the intensity of

crystallographic texture, revealed significant differences in grain orientation behaviour between the unmodified alloy and the boron-modified variants. For the unmodified alloy (Figure 6-21(a) – (d)), the texture index started relatively high at 59.45 for 30 μ s and gradually decreased with increasing exposure time, reaching a value of 13.24 at 120 μ s. Alongside the reduction in the texture index, the texture intensity also showed a marked decline, starting from 46.44 at 30 μ s, decreasing to 7.88 at 120 μ s. This reduction in both parameters indicated the grains developed a more uniform orientation, reducing anisotropy in the β -phase and resulting in a more randomized microstructure as exposure time increased. In contrast, for the amorphous boron-modified Ti6Al4V alloy (Figure 6-21(a') – (d')), the initial texture index at 30 μ s, which was 39.19, was already lower than that of the unmodified alloy, indicating less crystallographic alignment at the same laser scan speed. As exposure time increased, the texture index dropped significantly down to 3.52 at 120 μ s. The texture intensity followed a similar trend, starting at 49.10 at 30 μ s, and eventually reaching 4.30 at 120 μ s. The reductions in both texture index and intensity indicated a significant disruption of the crystallographic texture in the amorphous boron-modified Ti6Al4V alloy compared to the unmodified alloy. These findings suggested the addition of amorphous boron led to disruption of columnar grain and the formation of more equiaxed grains, resulting in a more randomized grain orientation. Similarly, the crystalline boron-modified alloy (Figure 6-21(a'') – (d'')) showed a strong initial texture at 30 μ s, calculated as 25.67, that decreased steadily to a very low value of 3.24 by 120 μ s. The crystalline boron modification resulted in even more pronounced texture weakening compared to the amorphous variant. The sharp decline in texture index and the more dispersed nature of the pole figures reflected the significant grain refinement and increased grain misorientation caused by the crystalline boron modification. While both boron-modified variants exhibited texture weakening as exposure time increases, the crystalline boron-modified alloy showed a more pronounced reduction in texture intensity compared to the amorphous boron variant. This indicates that crystalline boron was more effective at disrupting the initial texture and promoting equiaxed grain formation.

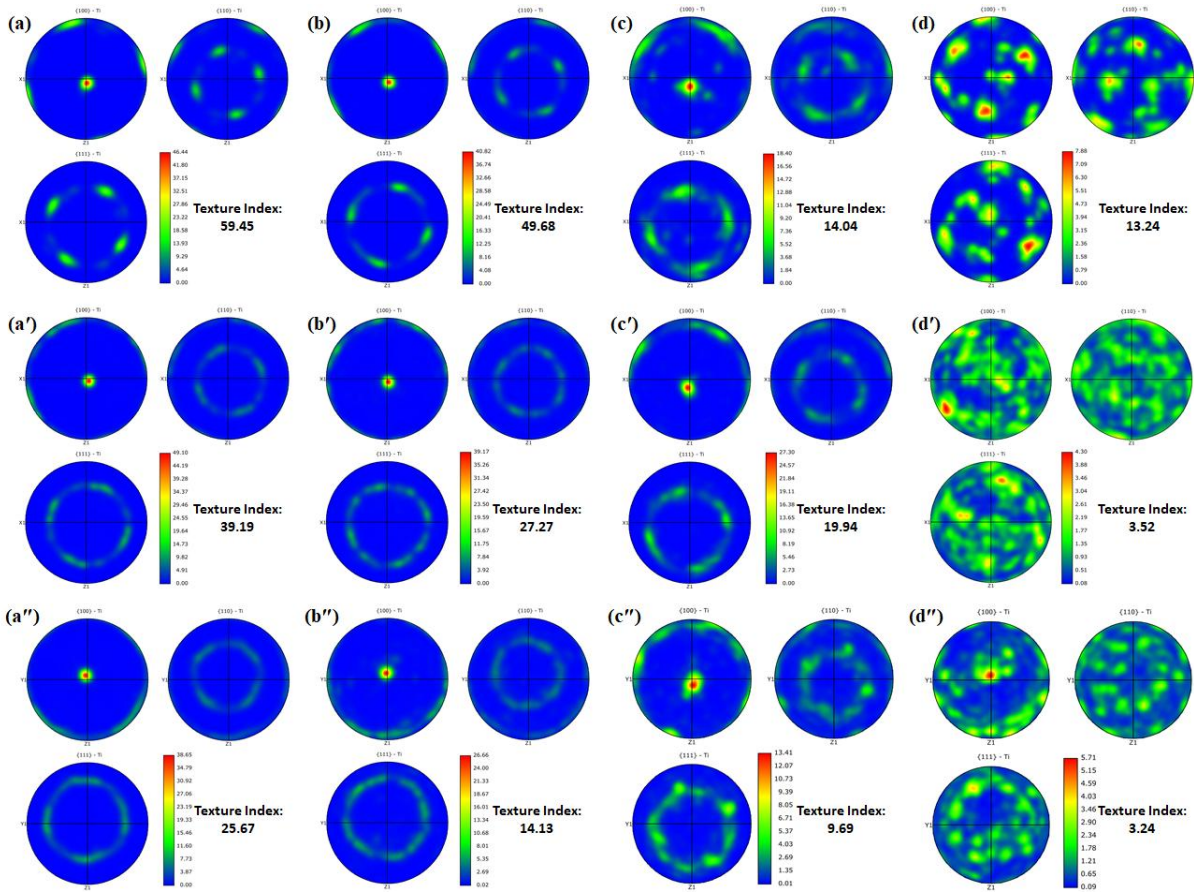


Figure 6-21 Pole figures of the reconstructed β -grains of Ti6Al4V and 0.1 wt.%B-modified Ti6Al4V alloys processed with 150W at different laser scan parameters. Images (a) to (d) represent Ti6Al4V alloy processed with exposure times ET30, ET60, ET90, and ET120, respectively. Images (a') to (d') show the corresponding hardness map for the alloy modified with amorphous boron under the same exposure conditions, while images (a'') to (d'') illustrate the maps for the alloy modified with crystalline boron under identical exposure parameters.

In the pole figures with rotated coordinates, one of the $\langle 100 \rangle$ poles in the reconstructed β -grains in the unmodified alloy (Figure 6-21(a)) was aligned nearly parallel to the longitudinal direction, indicating a strong preferred crystallographic orientation at 30 μ s. As the exposure time increased to 60 μ s (Figure 6-21(b)), the $\langle 100 \rangle$ poles remained largely parallel to the longitudinal direction, although the inclination of the other poles became more pronounced. By exposure time of 90 μ s (Figure 6-21(c)), a greater fraction of the $\langle 100 \rangle$ poles showed notable inclination, moving away from the longitudinal axis, with some poles having no specific orientation relationship to the longitudinal direction. At the highest exposure time, 120 μ s (Figure 6-21(d)), the $\langle 100 \rangle$ poles were highly dispersed, displaying significant misorientation and randomization, indicating a weakened texture and less alignment with the longitudinal direction. For the amorphous boron-modified alloy (Figure 6-21(a') – (d')), at 30 μ s and 60 μ s, the pole figures show a strong alignment of the $\langle 100 \rangle$ poles with the longitudinal direction. This indicates that a significant fraction of the $\langle 100 \rangle$ poles are aligned along the longitudinal axis at

these exposure times. However, at 90 μ s, a growing inclination of the $\langle 100 \rangle$ poles away from the longitudinal direction was present. This indicates that while some alignment remained, the $\langle 100 \rangle$ poles were starting to show more deviation. By 120 μ s, the pole figure displayed significant dispersion, with the $\langle 100 \rangle$ poles becoming more randomized. The loss of a clear central concentration of red dots and the broader scattering of poles indicated a substantial disruption in crystallographic alignment. The overall texture has weakened, and the $\langle 100 \rangle$ poles now showed random orientations with no significant alignment to the longitudinal axis. This transition from strong alignment at lower exposure times to randomization at higher exposure times highlighted the increasing grain misorientation and texture weakening as the exposure time increases in the amorphous boron-modified alloy. Similarly, the crystalline boron-modified Ti6Al4V alloy (Figure 6-21(a'') – (d'')) displayed a strong alignment of $\langle 100 \rangle$ poles with the longitudinal direction at 30 μ s and 60 μ s. However, as the exposure time increases to 90 μ s, the red spot shifts slightly off-centre, indicating the beginning of an inclination away from the longitudinal axis, with some poles deviating from their original alignment. At 120 μ s, a small fraction of the $\langle 100 \rangle$ poles remained aligned with the longitudinal direction, while the majority displayed a significant broadening and scattering of the $\langle 100 \rangle$ poles. This increased dispersion highlighted the growing misorientation and weakening of the preferred texture in the crystalline boron-modified alloy at longer exposure times. The loss of a concentrated central region and the scattered nature of the poles at 120 μ s indicated a strong deviation from the initial alignment, signifying a substantial disruption in the texture and crystallographic orientation compared to the earlier exposure times.

The pole figures of the reconstructed β -grains presented in Figure 6-22 provide insight into the texture evolution of Ti6Al4V and 0.1 wt.% B-modified Ti6Al4V alloys processed with 100W at varying laser scan parameters. The texture index values, measuring crystallographic alignment, highlighted significant differences between the unmodified and boron-modified alloys. For the unmodified alloy (Figure 6-22(a) – (e)), the texture index increased steadily with exposure time, starting at 6.40 for 120 μ s and reaching 21.59 by 450 μ s, indicating a strengthening of the texture over time. The texture intensity followed a similar trend, demonstrating the development of a more defined and aligned grain orientation as the exposure time increases. In contrast, the amorphous boron-modified alloy (Figure 6-22(a') – (e')) showed a much lower initial texture index of 2.41 at 120 μ s, which gradually increased to 2.91 at 450 μ s, but remained relatively weak compared to the unmodified alloy. The lower texture index and intensity across all exposure times indicated greater grain misorientation and a more randomized grain structure in the amorphous boron-modified alloy. The crystalline boron-modified alloy (Figure 6-22(a'') – (e'')) exhibited the lowest texture index values, starting at 1.82 at 120 μ s and reaching only 2.96 by 300 μ s, followed by a slight decline to 2.24 at 450 μ s. The weak texture development and increased grain dispersion suggested that crystalline boron modification led to greater grain misorientation, and less crystallographic alignment compared to the amorphous boron-modified and unmodified alloys.

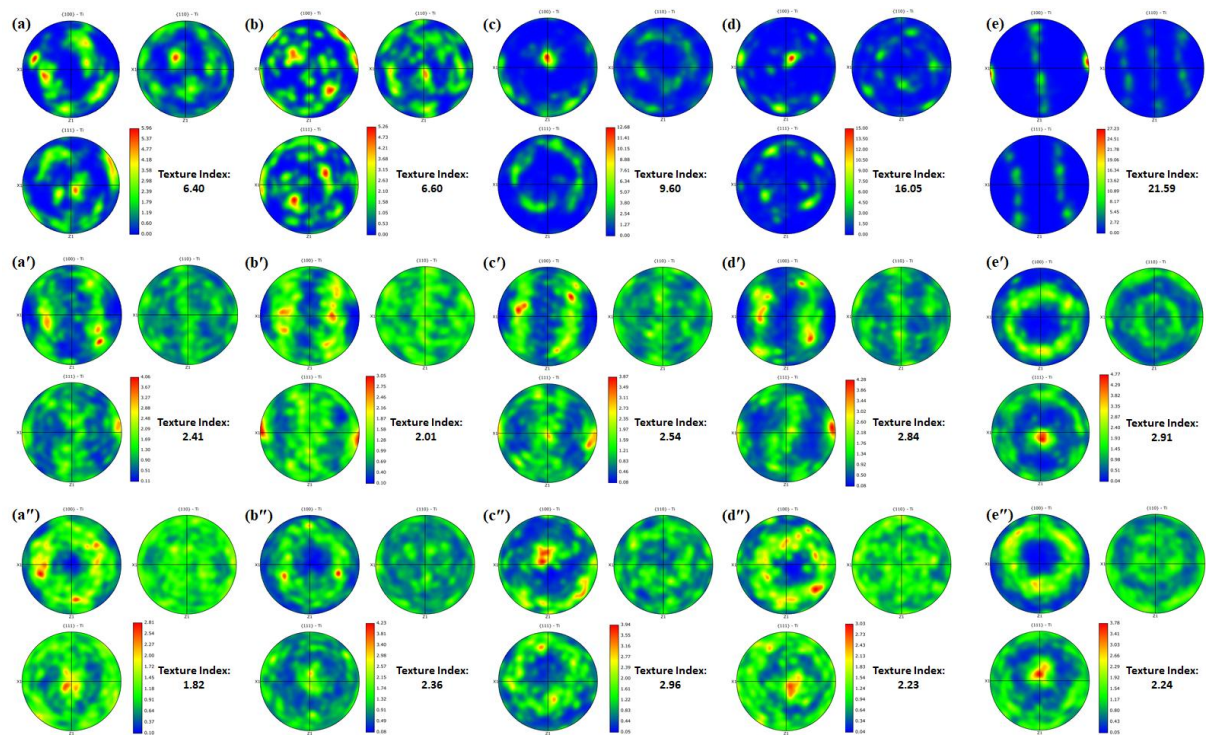


Figure 6-22 Pole figures of the reconstructed β -grains of Ti6Al4V and 0.1 wt.%B-modified Ti6Al4V alloys processed with 100W at different laser scan parameters. Images (a) to (d) represent Ti6Al4V alloy processed with exposure times ET120, ET180, ET225, ET300 and ET450, respectively. Images (a') to (d') show the corresponding hardness map for the alloy modified with amorphous boron under the same exposure conditions, while images (a'') to (d'') illustrate the maps for the alloy modified with crystalline boron under identical exposure parameters.

In the pole figures with rotated coordinates for the unmodified alloy (Figure 6-22(a) – (e)), the $\langle 100 \rangle$ poles showed a clear evolution of texture with increasing exposure time. At 120 μ s, the $\langle 100 \rangle$ poles exhibited some concentration near the centre of the pole figure, indicating a moderate alignment with the longitudinal direction. However, the presence of red spots away from the centre suggested there was already some inclination of the grains, indicating a mixed texture with partial misorientation. As the exposure time increases to 180 μ s, grains started to align $\langle 100 \rangle$ poles, but some broadening of the distribution was also observed. This indicates that while most grains remained aligned with the longitudinal direction, there was a slight increase in grain misorientation. By 225 μ s, the texture became more pronounced. The $\langle 100 \rangle$ poles show a strong alignment, but with slight inclination. Further increase in exposure time to 300 μ s, the texture intensity increased even further, as indicated by a clearer concentration of $\langle 100 \rangle$ poles, indicating the grains were still well-aligned along the $\langle 100 \rangle$ axis with only slight deviation from the longitudinal direction, resulting in a continued strong texture. With 450 μ s, the $\langle 100 \rangle$ poles maintained strong alignment with a slight inclination from the longitudinal direction. The texture was still well-developed, as the grains were concentrated but slightly shifted, reflecting minimal misorientation. The grains remained primarily aligned in the $\langle 100 \rangle$ direction. For the amorphous boron-modified alloy (Figure 6-22(a') – (e')), at 120 μ s and 180 μ s,

a small fraction of the $\langle 100 \rangle$ poles were aligned with the longitudinal direction, but the majority displayed broader inclination. As the exposure time increased to 225 μs , the $\langle 100 \rangle$ poles became more inclined, deviating further from the longitudinal axis. By 300 μs and 450 μs , the pole figures showed considerable dispersion, indicating significant grain misorientation. The broad scattering of the $\langle 100 \rangle$ poles suggested a loss of crystallographic alignment and a weakening of texture as exposure time increased. Similarly, the crystalline boron-modified alloy (Figure 6-22(a'') – (e'')) displayed a small concentration of $\langle 100 \rangle$ poles aligned with the longitudinal direction at 120 μs and 180 μs , but with greater inclination and scattering compared to the amorphous variant. At 225 μs and 300 μs , the $\langle 100 \rangle$ poles showed further dispersion, moving away from their original alignment, and by 450 μs , the $\langle 100 \rangle$ poles were highly randomized, indicating a substantial disruption of the texture. The increased misorientation and broadening of the poles at higher exposure times highlight the greater influence of crystalline boron in weakening the crystallographic texture.

The pole figures of reconstructed β -grains presented in Figure 6-21 and Figure 6-22 revealed clear trends in the texture evolution of Ti6Al4V and 0.1 wt.%B-modified Ti6Al4V alloys processed under various laser conditions. Overall, the unmodified alloy exhibited higher initial texture indices changing with longer exposure times, whereas both amorphous and crystalline boron-modified variants showed consistently lower texture indices. This indicates that boron addition promoted increased grain misorientation and a more randomized orientation distribution compared to the base alloy. It is important to note, however, that a few of the samples analysed had relatively low numbers of β -grains in the regions measured by EBSD. Consequently, the resulting pole figures and texture indices, especially for those samples with fewer grains, may not fully capture the complete texture of the bulk material. When the grain count is low, local variations in grain orientations can disproportionately affect the calculated texture intensity or index. Despite these potential sampling limitations, the overall patterns remain indicative of the main microstructural transformations observed—for example, the significant disruption of columnar grains and increased grain boundary area associated with boron additions. Even with these limitations, the pole figures in Figure 6-21 demonstrated that at a higher laser power of 150 W, texture weakening in boron-modified alloys becomes more pronounced as exposure time increases. Similarly, in Figure 6-22, processed at lower power of 100 W, the unmodified alloy develops a stronger texture over certain ranges of exposure time, whereas the boron-modified alloys maintain a more randomized microstructure. Thus, although caution is advised in interpreting the exact numerical values of the texture indices in these samples with fewer grains, the trends observed—such as reduced overall crystallographic alignment in boron-modified alloys—remain valid indicators of how boron additions affect microstructure evolution.

6.8 Discussion

6.8.1 Print Quality

The introduction of nanoparticles alters the thermophysical properties of the base metal, necessitating changes in the processing parameters to produce high-quality, defect-free parts. Generally, nanoparticles like boron exhibit a higher laser absorption coefficient than titanium, resulting in more efficient energy absorption during printing (Fereiduni et al., 2019). Additionally, exothermic reactions between the boron nanoparticles and the metal matrix contribute extra heat to the melt pool, affecting its overall energy balance. When nanoparticles adhere to the surfaces of larger metal powder particles, they increase surface roughness, which, in turn, reduces laser reflectivity (Fereiduni et al., 2019; D. He et al., 2023). These nanoparticles can also help bridge gaps between metal particles, promoting consolidation in theory (J. A. Otte, Zou, et al., 2022). While one might expect the addition of nanoparticles to simplify the printing process, it is often found that nanoparticle-micron powder mixtures actually demand a higher energy density than pure metals or alloys. This is largely because many nanoparticles are thermally stable and possess melting points significantly higher than that of the base metal (Essien & Vaudreuil, 2022). The presence of unmelted particles interferes with melt pool dynamics, significantly impacting its shape and the final consolidation of the printed part (Y. He et al., 2019).

Although the risk of print defects was anticipated, it was initially chosen to process the Ti6Al4V-0.1B powders using the standard printing parameters typically employed for Ti6Al4V. This decision was made for a few reasons. Firstly, it mirrors common industrial practice, where most printing equipment comes as “black boxes” with built-in, proprietary “parameter sets” fine-tuned by the manufacturer for commonly used metals and alloys (National Institute of Standards and Technology, 2013). Usually, the options are limited to a few materials, such as stainless steels, CP-Ti, Ti6Al4V alloys, and copper. Consequently, when presented with a new material like the Ti6Al4V-0.1B powder blend, operators would probably have to select from the pre-existing parameters, with Ti6Al4V being a reasonable choice. Secondly, from a research perspective, using the same printing conditions for both materials were essential to isolate the impact of boron addition. Furthermore, applying parameters optimized for titanium to Ti6Al4V-0.1B serves as a logical baseline for refining the printing conditions for this new material. It is worth noting that the work done by other researcher provides an in-depth optimization of printing parameters for Ti6Al4V-0.1B alloys similar to the composition under consideration here. However, these parameters were tailored to a specific printer, making them unsuitable for direct application to different equipment, as it is well-known that the same material requires different settings on different printers (Sola et al., 2023). In summary, the occurrence of cracks in the Ti6Al4V-0.1B parts, as illustrated in Figure 6-23, was not entirely surprising. While adding boron offers benefits for the microstructural design of titanium-based PBF-LB/M components, the challenge of defining appropriate processing parameters and the difficulty in adapting them to printers that function as “black boxes” present a significant barrier to the broader use of boron-modified feedstocks in the industry.

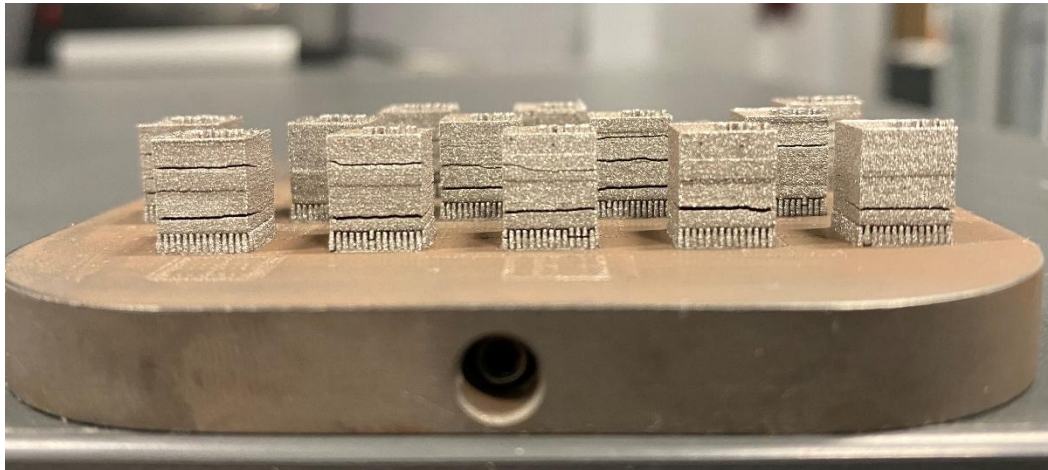


Figure 6-23 Ti6Al4V-0.1B parts that are mainly cracked before being separated from the build platform.

6.8.2 Densification Behaviour

The reduction in pore content observed in PBF-LB/M produced Ti6Al4V and Ti6Al4V-0.1B alloys using 100 – 150W laser power and extended exposure times up to 450 μ s, despite operating in the keyhole regime, highlights the critical role of keyhole stability and controlled energy density in mitigating defect formation. Cross-sectional analysis confirming keyhole-mode melt pools, characterized by deep, narrow vapor depressions, initially appears counterintuitive, as keyhole dynamics are often linked to porosity from turbulent collapse and gas entrapment (Khairallah et al., 2016). However, the combination of lower power and longer exposure times likely stabilizes the keyhole, avoiding the chaotic fluctuations typical of high-power regimes. At 100 – 150W, the recoil pressure generated by vaporization is insufficient to excavate an excessively deep or unstable keyhole, instead creating a shallower vapor cavity that remains open long enough for gases to escape through the keyhole channel before solidification—a mechanism corroborated by Guo et al. (L. Guo et al., 2023), who observed that stable keyholes act as venting pathways for trapped gases. This contrasts with high-power PBF-LB/M (>300W), where violent keyhole oscillations and collapse events trap argon, nitrogen, or vaporized contaminants, producing irregular pores (Bayat et al., 2019).

The extended exposure times in the experiments further enhance stability by allowing the keyhole to maintain a steady-state equilibrium. As demonstrated by Cunningham et al. (R. Cunningham et al., 2019), keyhole stability is governed not only by laser power but also by the interaction time between the beam and the material. Longer exposure times reduce the velocity of keyhole wall fluctuations, minimizing the risk of localized collapse and gas entrapment. This aligns with the findings, where the controlled energy input by the combination of lower power and longer exposure times achieves a balance between keyhole penetration and stability, effectively venting gases while avoiding the "keyhole porosity" typically reported in high-speed, high-power processes. Additionally, the reduced thermal gradients associated with

longer exposure times may suppress pore nucleation mechanisms. For instance, slower cooling rates allow dissolved hydrogen (a common pore-forming gas in metals like titanium or aluminium) to diffuse out of the melt pool rather than becoming trapped at solidification fronts, as noted by Tammias-Williams et al. (Tammias-Williams et al., 2015, 2017). This dual effect of gas venting through a stable keyhole and suppressed gas nucleation explains the paradoxical reduction in porosity despite keyhole-mode melting. Importantly, obtained results challenge the conventional dichotomy between "conduction mode = low porosity" and "keyhole mode = high porosity," instead emphasizing that keyhole stability—not merely operational regime—determines defect outcomes. This finding resonates with recent work by Zhao et al. (C. Zhao et al., 2020), who demonstrated that even shallow keyholes can minimize porosity if maintained in a stable state, and Leung et al. (Leung et al., 2018), who linked keyhole oscillations to pore formation thresholds. However, this study advances this understanding by showing that lower power (100 – 150W) can achieve sufficient keyhole stabilization when paired with extended exposure times, avoiding the need for complex modulation strategies (e.g., beam shaping). Trade-offs persist, such as reduced build rates and potential limitations in melt pool overlap consistency, but these are offset by the exceptional density achieved in Ti6Al4V, which surpasses typical as-printed PBF-LB/M components (King et al., 2015).

6.8.3 Evolution of Lamellar α/β Structure

Due to the rapid solidification and high cooling rates in PBF-LB/M, Ti6Al4V commonly forms a brittle martensitic α' phase. This has prompted research efforts aimed at promoting the breakdown of α' into α and β phases (Facchini et al., 2010; L. E. Murr et al., 2009; Vilaro et al., 2011; W. Xu et al., 2015, 2017). It has been demonstrated that increasing the focus offset distance (FOD) and layer thickness to more than 50 μm can facilitate in-situ decomposition of the martensite, resulting in an ultrafine α/β lamellar structure that exhibits enhanced ductility and strength (W. Xu et al., 2015, 2017). Nevertheless, adjusting these two parameters can negatively affect product resolution, and thicker layers may increase the likelihood of pore formation (Abd-Elghany & Bourell, 2012). Moreover, there is no conclusive evidence showing that modifying FOD is a crucial factor for α' decomposition, largely because of a lack of comprehensive characterization and analysis of how martensitic α' evolves into α/β lamellae, as well as insufficient understanding of the specific conditions that lead to this transformation.

Figure 6-24(a) – (c) demonstrate how the martensitic α' phase decomposes into α/β lamellae. Figure 6-24(b) presents the thermal cycles for point 1 shown in Figure 6-24(a), drawing on insights from earlier research (Tran et al., 2017; J. Yang et al., 2016). According to finite element analysis (Roberts et al., 2009), this thermal cycle can be considered representative of the entire layer since similar thermal conditions occur uniformly across the same layer. Initially, the temperature rises above the liquidus temperature (T_L) as a new layer is added on top of the previous layers. This is followed by rapid cooling to below the martensite start temperature (M_S) at a rate exceeding 10^6°C/s (I. Gibson et al., 2020; J. Yang et al., 2016), leading to the formation of a martensitic α' structure in the first layer. As more layers (from layer 2 to X) are

added, the temperature at point 1 gradually increases until it reaches a steady state temperature (T_{SS}). This state is achieved when the heat input from newly deposited layers balances the heat dissipation into the layers beneath, maintaining a constant temperature for a specific period (Δt). Although the precise number of layers required to reach T_{SS} is uncertain, it is estimated to be fewer than about 6–10 layers. This estimation is based on the observed thickness (approximately 200–300 μm) of the top regions in samples, where the acicular α' structure dominates (as seen in Figure 6-9 to Figure 6-12). This thickness is roughly 6–10 times the individual layer thickness of around 30 μm . Once the steady state is achieved, the temperature decreases as the rate of heat input drops below the rate of heat dissipation. If T_{SS} exceeds the α' decomposition temperature (T_D , approximately 600–850°C for Ti6Al4V (S. Cao et al., 2018; X. Tan et al., 2016; W. Xu et al., 2017)), the α' in the first layer will transform into α/β after the deposition of an additional n layers (as illustrated in Figure 6-24(c)). Depositing another layer beyond this point will cause the second layer to convert into α/β , eventually transforming the entire sample into α/β , with the exception of the topmost 6–10 layers.

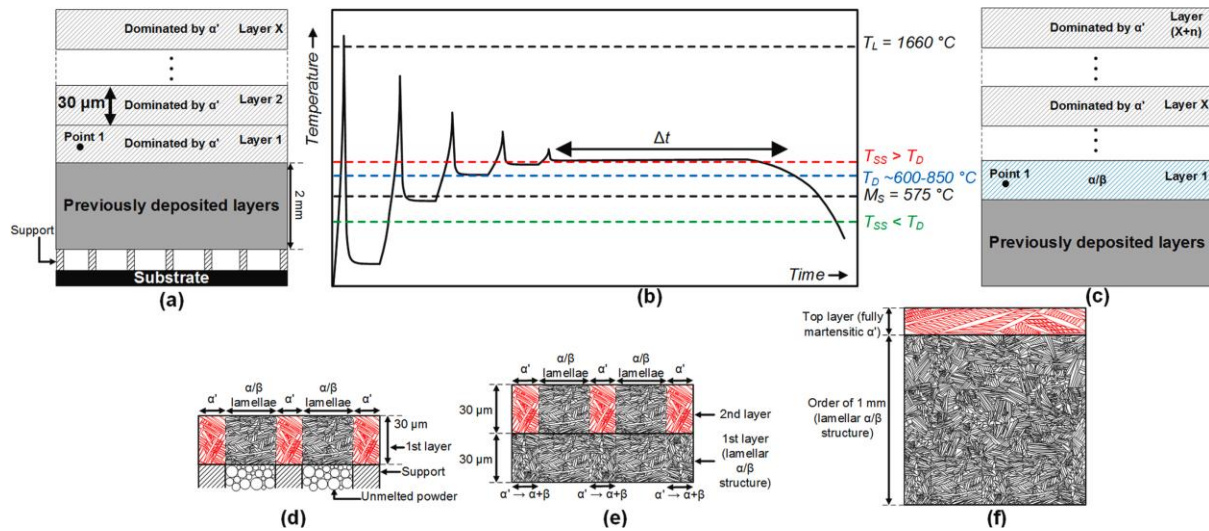


Figure 6-24 Schematics of α/β formation during SLM: (a) Sequential α' layers forming on a thick deposit; (b) Thermal cycles at point 1 in layer 1, showing rapid temperature changes with decreasing amplitude until reaching a steady state (T_{SS}) for Δt ; (c) Transformation of layer 1 from α' to α/β after n layers post layer X. Microstructure evolution in boron-modified alloy: (d) First layer showing α/β lamellae on unmelted powder and α' on supports; (e) Second layer decomposing α' in the first; (f) Newly formed top layer as martensitic α' over a fully decomposed deposit.

When the T_{SS} is lower than the T_D , the structure primarily consists of acicular α' , though partial decomposition may occur down to a T_{SS} of approximately 400°C, as noted by Mur et.al. (Gil Mur et al., 1996). The presence of lamellar α/β in boron-modified alloy samples indicates that the T_{SS} is around 600–850°C, achieved when the speed (v) is below approximately 1000 mm/s, and the energy (E) is above $\sim 83 \text{ J/mm}^3$. In unmodified alloy samples, where the energy is close to 83 J/mm^3 , the T_{SS} likely does not exceed 600°C, or the time (Δt) is too short, resulting in

partial decomposition into β lamellae in some isolated regions. At even lower energy levels, the decomposition of α' is entirely suppressed.

As highlighted in Section 6.5, the formation and evolution of microstructure in samples during the initial few layers appear to be influenced by their location within the support structure—specifically, whether they rest on solid legs or unfused particles, as summarized in Figure 6-24(d) – (f). Unlike layer 1 in Figure 6-24(a), deposited on existing layers and consists entirely of α' martensite, martensitic plates in the single layer only develop on the solid legs, while α/β lamellae form on the loose powder (Figure 6-24(d)). When a second layer is deposited (Figure 6-24(e)), its microstructure mirrors that of the single layer (Figure 6-24(d)). However, this deposition triggers the decomposition of all previously formed α' in the first layer into α/β (Figure 6-24(e)). After a sufficient number of layers—around 30, or roughly 1 mm in height—the newly added top layer will consist solely of α' (Figure 6-24(f)), similar to what is seen in Figure 6-24(a). The formation of α/β lamellae on top of unmelted powder is largely due to the much lower thermal conductivity (Neira-Arce, 2012) and higher laser absorption of unfused powder compared to solid support material (Kruth et al., 2003; Boley et al., 2016). This increased laser energy absorption causes the unmelted powder bed to reach higher temperatures than the solid support. The combination of low thermal conductivity and heat build-up results in greater heat retention and reduced dissipation. However, it is unlikely that the high cooling rate during PBF-LB/M, typically over 10^6 °C/s, could drop to below 20 °C/s, the rate needed to form α/β directly from the prior β phase (Ahmed & Rack, 1998). Consequently, α' likely forms initially before decomposing in the first track, but it gets reheated by subsequent tracks, undergoing thermal cycles similar to those in layer 1 (as seen in Figure 6-24(a)). This reheating causes the α' to decompose into α/β . Essentially, the heat required to raise the temperature above T_D in the first track is provided by the following laser tracks in that same layer. On the other hand, the solid support's higher heat transfer rate keeps T_{SS} well below T_D or only allows brief periods above T_D , leading to the formation of martensitic α' over the solid supports. In this case, only one additional layer is needed to prompt decomposition into α/β , unlike the ~6–10 layers required when the entire substrate is solid (see Figure 6-24(a)). These effects from the unmelted powder disappear once the layer thickness reaches around 1 mm.

6.8.4 Boron-driven Microstructural Refinement Mechanism

In PBF-LB/M, various processing parameters can be adjusted to promote the development of fine, equiaxed grains. Factors such as grain shape, size, and texture are largely influenced by the thermal conditions present during solidification, while the resulting microstructure depends on the cooling rate after solidification. Key elements like laser power, spot size and shape, and traverse speed significantly impact the thermal history, thereby affecting the final microstructure (Kobryn & Semiatin, 2001). Despite these efforts, achieving equiaxed microstructures remains challenging without introducing nucleant particles (Todaro et al., 2020). One promising method involves applying high-intensity ultrasound during the solidification process, which can alter the microstructure of the resulting crystalline material.

This ultrasonic grain refinement technique has been effectively demonstrated for Ti6Al4V (Todaro et al., 2020). Unlike chemical modifications, this approach preserves the purity of the metal powder, though it does necessitate specialized equipment to integrate ultrasonic vibration with AM. Post-printing heat treatments can be employed to modify the distribution, size, and morphology of the α phase, but they generally have a minimal impact on prior- β grains (Kobryn & Semiatin, 2001). Alternatively, adding boron offers an effective means to achieve grain refinement and limit columnar grain growth. Boron influences both prior- β grains and α laths without requiring any specialized printing hardware (Sola & Trinchi, 2023). Notably, even trace quantities of boron are sufficient to modify the microstructure of titanium and its alloys, minimizing the risk of agglomeration of additives in the melt pool while meeting strict chemical specifications, such as those outlined in ASTM F2924 (ASTM International, 2021) for Ti6Al4V parts produced through PBF.

The addition of boron during solidification increases the freezing range of the alloy, contributing to the directionality of the surface columnar grains. As calculated by JMatPro in Chapter 4, the freezing range for hypoeutectic trace-boron alloys is about 230K (ranging from 1943K to 1813K). In contrast, Ti6Al4V has a much narrower freezing range of approximately 13K, causing it to behave similarly to a pure metal during solidification, where it nucleates epitaxially from previous layers and solidifies rapidly. The influence of the solidification range on the evolved β -grain morphology is illustrated in Figure 6-25. Figure 6-25(a) schematically shows the solidification process of Ti6Al4V having a very narrow solidification range and constitutional undercooling. These solidification conditions promote epitaxial growth of β columnar grains. Nevertheless, trace amount of B addition extends the solidification range and constitutional undercooling zone (Figure 6-25(b)). Due to the limited solubility of boron in solid titanium, boron is rejected into the liquid during solidification. The lateral rejection of boron-rich solute from the base and sides of columnar dendrites restricts lateral growth and provides an opportunity for neighbouring dendrites to grow.

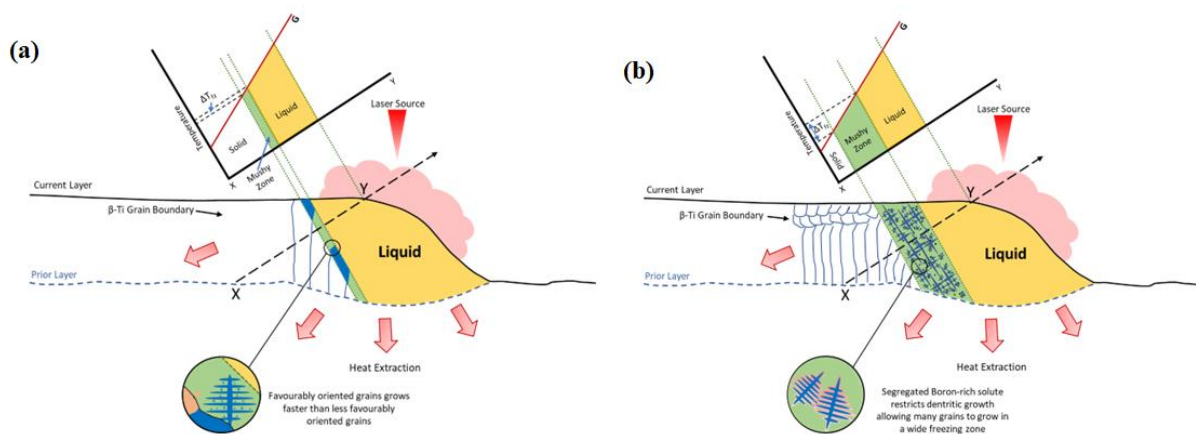


Figure 6-25 A side-view schematic illustrating how the increased freezing range (ΔT_f) due to the presence of boron extends the solid + liquid (mushy) zone and encourages the development of curved columnar grains in boron-containing alloys. The diagram assumes a constant temperature gradient (G)

and cooling rate for both alloys. In Ti6Al4V, ΔT_{fr} is approximately 13K, whereas boron additions increase it to around 230K. Schematic (a) represents boron-free Ti6Al4V, while (b) shows Ti6Al4V with trace boron additions.

The final microstructure is influenced by the volume fraction of equiaxed grains. According to Hunt (Hunt, 1984), if the volume fraction is below 0.66%, equiaxed grains become part of the growing columnar structure, resulting in fully columnar grains. If it exceeds 49%, equiaxed grains block the growth of columnar grains, forming a fully equiaxed structure. In the case of trace boron addition, the volume fraction typically falls between these values, resulting in a mixed microstructure of short columnar dendrites and equiaxed grains. Further increases in boron content do not significantly restrict grain growth due to the saturation of the growth restriction effect, and excessive boron may even harm the mechanical properties.

With this understanding of how boron influences solidification and microstructure, the solidification process based on the Ti–B phase diagram shown in Figure 4-31 in this study can be outlined as follows: Liquid $\rightarrow$ Liquid + primary β -titanium $\rightarrow$ primary β -titanium + eutectic (TiB + β -titanium) $\rightarrow$ (α -titanium + β -titanium + TiB). Due to the variation in cooling rates between the bottom and middle regions of the molten pool, this sequence of solidification occurs first in the bottom region, followed by the middle. An overview of the formation mechanism for both dendritic (columnar) and equiaxed network structures is illustrated in Figure 6-26. When the temperature of the molten pool falls to the liquidus point, primary β grains begin to nucleate at the bottom of melt pool, forming a stable equilibrium solidification temperature curve (T_e , Figure 6-26(a)). As the primary β -grain grows further, boron atoms are pushed into the surrounding liquid due to their extremely low solubility in the titanium matrix (0.43 at.% in β -titanium and 0.2 at.% in α -titanium) (Attar, Bönisch, Calin, Zhang, Scudino, et al., 2014). This results in an accumulated boron zone ahead of the solidification front, which in turn creates a constitutional supercooling (CS) zone (P. Wang et al., 2010). This CS zone lies in the overlap between the temperature gradient (G) curve and the T_e curve. As solidification progresses, the primary β grain continues to grow epitaxially, forming columnar grains while boron atoms accumulate at the grain boundaries. When the molten pool cools down to the eutectic temperature in the bottom region, a eutectic reaction takes place, leading to the formation of TiB whiskers along the grain boundaries, which contribute to the creation of the columnar or dendritic network structure.

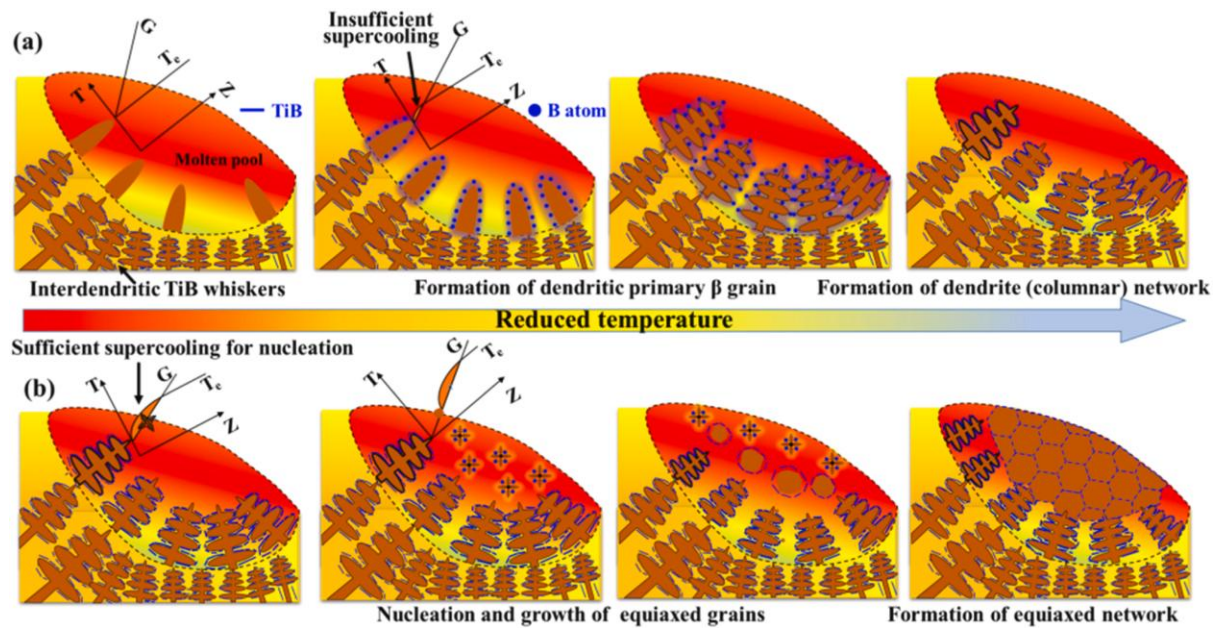


Figure 6-26 A schematic illustrating the formation process of (a) a dendritic (columnar) network structure and (b) an equiaxed network structure.

During the final stages of the solidification process, the significant decrease in temperature gradient and the diminished Marangoni convection (M. Fang et al., 2021) allowed for the accumulation of boron at the tips of the primary β grains. This situation created a broad overlap between the temperature gradient and the eutectic temperature curve, which facilitated adequate constitutional supercooling and encouraged the nucleation of β grains (as illustrated in Figure 6-26(b)). Consequently, equiaxed β grains began to nucleate and grow continuously above the dendritic or columnar β grains, leading to a notable transition from dendritic to equiaxed grains, as well as grain refinement. As the temperature dropped further to reach the eutectic point, the eutectic reaction triggered, resulting in the formation of TiB at the boundaries of equiaxed grains and creating an interconnected network structure.

While the interdependence theory provides a useful framework for understanding the CET transition, it does not fully account for all the mechanisms that govern CET, particularly in alloys modified with elements like boron. This theory primarily focuses on the competition between nucleation and growth dynamics in the melt. However, atomic matching plays an equally critical role in facilitating the CET. The atomic-scale matching between the nucleating phase (e.g., boron particles) and the solidifying alloy (e.g., titanium) can significantly enhance nucleation efficiency. This atomic match, or "edge-to-edge matching," lowers the nucleation barrier by providing a more energetically favourable surface for new grains to form. Without this atomic compatibility, even an abundance of nucleation sites as suggested by interdependence theory might not be sufficient to induce a full transition to equiaxed grains. Therefore, both interdependence theory and atomic matching must be considered to fully explain CET, especially in complex alloy systems. Boron is likely present in its elemental form

in the melt and could act as a nucleation site before the formation of TiB particles, which occurs after the completion of the β transformation. Some TiB particles were found within the prior- β grains and if boron act as nucleation sites during solidification, there should have a certain orientation relationship between boron and β -titanium phase. To determine if crystalline boron acts as an effective nucleating agent, the edge-to-edge matching (E2EM) model (Qiu et al., 2009) was used to evaluate the crystallographic alignment between β -titanium and boron. Figure 6-27(a) and (b) shows the atomic configurations of the most close-packed planes of β -titanium and boron, respectively. The β -titanium and boron phases are body-centered cubic and rhombohedral, respectively. The interatomic spacings of the close-packed rows are 0.229 nm along the $[11\bar{1}]_\beta$ direction in the $(011)_\beta$ plane and 0.248 nm along the $[0\bar{1}0]_B$ direction in the $(005)_B$ plane. The misfit f_r between them is 8.30%, which is slightly below the empirical threshold of 10% (M. X. Zhang et al., 2005), suggesting an orientation relationship can form between the two phases. Based on E2EM model, it is likely that some crystalline boron particles serve as nucleation sites and are more effective than any impurities present in the base alloy, as impurities alone did not result in the formation of equiaxed grains. Hence, these crystalline boron particles act as the heterogeneous nuclei for the equiaxed prior- β grains during solidification. This atomic matching can also be the reason why amorphous boron-modified alloys showed larger equiaxed grains compared to their crystalline counterparts. Although CET occurred in the amorphous boron-modified alloy, it was less pronounced because amorphous boron lacks the crystallographic structure needed for effective edge-to-edge matching with the β -titanium phase. Without this precise atomic alignment, the nucleation efficiency is reduced, leading to fewer nucleation sites and, consequently, larger equiaxed grains in the final microstructure. Therefore, the presence of crystalline boron results in a more effective CET and a finer grain structure.

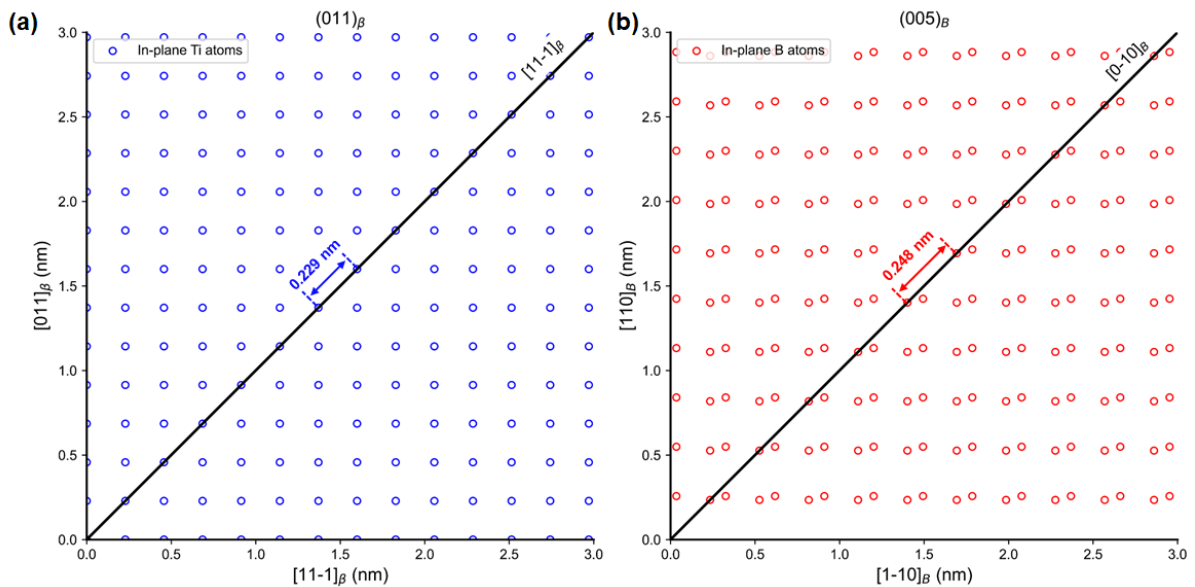


Figure 6-27 The atomic configuration in the close packed plane of (a) $(011)_\beta$ and (b) $(005)_B$. A pair of matching close packed rows are highlighted by bold solid lines.

6.8.5 Influence of Boron Additions on the Texture Reduction

In Ti6Al4V without boron, the texture indexes in the analysed regions were significantly higher compared to the 0.1 wt.% boron-modified alloy. Although the evaluated areas in Ti6Al4V included only a limited number of prior- β grains, which artificially inflated the texture indexes, it is clear that the texture in Ti6Al4V was quite pronounced, a fact widely supported by the literature (S. S. Al-Bermani et al., 2010; A. A. Antonysamy et al., 2013). On the other hand, the boron-modified alloy exhibited a noticeable decrease in texture intensity, indicating a much weaker texture. Furthermore, variations in laser scanning parameters caused the texture to weaken even more.

The limited number of transformed α laths that share specific orientation relationships with the TiB particles suggests the reconstructed β phase results are reliable. Without boron, the epitaxially grown β grains are quite large, with their (100) planes aligned perpendicularly to the thermal gradient, which corresponds to the build direction in the PBF-LB/M process (S. S. Al-Bermani et al., 2010). This results in a strong $\langle 100 \rangle_{\beta} // Z$ -axis texture in the β phase, a characteristic also observed in Ti6Al4V where the (100) planes are aligned with the building direction (A. A. Antonysamy et al., 2013). However, the addition of boron significantly reduces this $\langle 100 \rangle_{\beta} // Z$ -axis texture. In both the amorphous and crystalline boron-modified alloys, the local texture remains quite sharp, but only some of the (100) planes align perpendicularly to the building direction, as shown in the pole figures of these samples. On the other hand, the texture in the crystalline boron-modified alloy becomes very weak, with no identifiable $\langle 100 \rangle_{\beta} // Z$ -axis texture. This texture weakening is linked to the formation of equiaxed grains, although a full columnar-to-equiaxed transition did not occur, as all the alloys still contain some columnar grains. The larger freezing range along the laser track in boron-modified Ti6Al4V prolongs the solidification time, making epitaxial growth along the building direction less favourable. Furthermore, the potential lattice mismatch between the β -titanium phase and crystalline boron promotes the growth of β grains towards the centre of the molten pool. Consequently, the $\langle 100 \rangle_{\beta} // Z$ -axis texture that forms during solidification is reduced in the amorphous boron-modified alloy and nearly completely eliminated in the crystalline boron-modified alloy.

It is well established that the orientations of secondary α laths, transformed from two neighbouring prior- β grains with common $\{110\}$ poles, follow the variant selection mechanism (Bhattacharyya et al., 2003; Germain et al., 2008; G. C. Obasi, Biroscas, Leo Prakash, et al., 2012; Stanford & Bate, 2004; van Bohemen et al., 2008). Specifically, when the misorientation between the $\{110\}$ poles of adjacent β grains is less than 10° , the (0001) poles of the transformed secondary α laths that precipitate from the grain boundary between these β grains are likely to align (G. C. Obasi, Biroscas, Quinta Da Fonseca, et al., 2012; van Bohemen et al., 2008). In unmodified alloy sample, the solidified β phase exhibits a strong texture, increasing the likelihood of neighbouring β grains having common $\{110\}$ poles. As shown in the EBSD results for the reconstructed β phase, the $\{110\}$ poles of the β grains are highly aligned, with the angular distance between the $\{001\}$ poles in β_1 and β_2 being less than 10° , and less than 5°

between β_2 and β_3 . Consequently, the α phase transformed from the common β grain boundaries tends to share similarly oriented (0001) poles, resulting in a strong α texture. In the analysed areas of unmodified alloy, which include multiple prior β grains, the α texture is notably strong with common (0001) poles. In contrast, the $\{110\}$ poles of the reconstructed β grains in Ti6Al4V with boron additions show scatter, likely due to the weakening of the $\langle 100 \rangle_{\beta} // Z$ -axis texture. As a result, the likelihood of neighbouring β grains sharing common $\{110\}$ poles is much lower, reducing the extent of variant selection during the α precipitation process. This leads to a weaker transformed α texture in boron-modified Ti6Al4V alloy compared to unmodified Ti6Al4V. Additionally, the nucleation of the α -phase from TiB particles further weakens the texture, as strong orientation relationships between α and TiB were observed (details given in Chapter 4), although this effect does not apply to all α lamellae.

6.8.6 Inhibiting Grain Growth TiB During Post-Deposition Thermal Cycle

In boron-modified Ti6Al4V samples, the addition of boron leads to the in-situ formation of TiB particles during the solidification process. These TiB particles can exist in two forms: primary TiB, which forms directly from the melt, and secondary TiB, which can precipitate during subsequent thermal cycles. The repeated thermal cycling during processes such as PBF-LB/M, especially in the keyhole regime, provides the necessary conditions for boron atoms to diffuse within the matrix and nucleate as secondary TiB particles. These thermal cycles allow the redistribution of boron and its precipitation as fine TiB particles within the grain interiors. The presence of these TiB particles significantly influences the microstructural evolution and grain boundary dynamics of the alloy. TiB particles, when distributed along grain boundaries, can trigger the Zener pinning mechanism (Tamirisakandala & Miracle, 2012), effectively hindering grain boundary migration. As seen in Figure 6-28, At temperatures within the β -transus and recrystallization ranges, the migration of the α -phase boundaries is obstructed by the secondary TiB particles dispersed within the grain. This hindrance in boundary movement prevents the formation of coarse α -titanium colonies by suppressing the micro- α lamellar recrystallization. When the thermal cycle temperature exceeds the β -transus temperature, the primary TiB particles play a crucial role. These particles impede the migration of β -phase boundaries, limiting the growth of prior- β grains during high-temperature exposure. Consequently, this restriction in grain growth helps avoid the formation of coarse transformation microstructures during cooling. In contrast, in Ti6Al4V without boron modification, the grain boundaries of both α and β phases are clean and free from obstacles like TiB particles. This absence of hindrances at the grain boundaries facilitates easy grain boundary migration, leading to significant grain coarsening during thermal cycle.

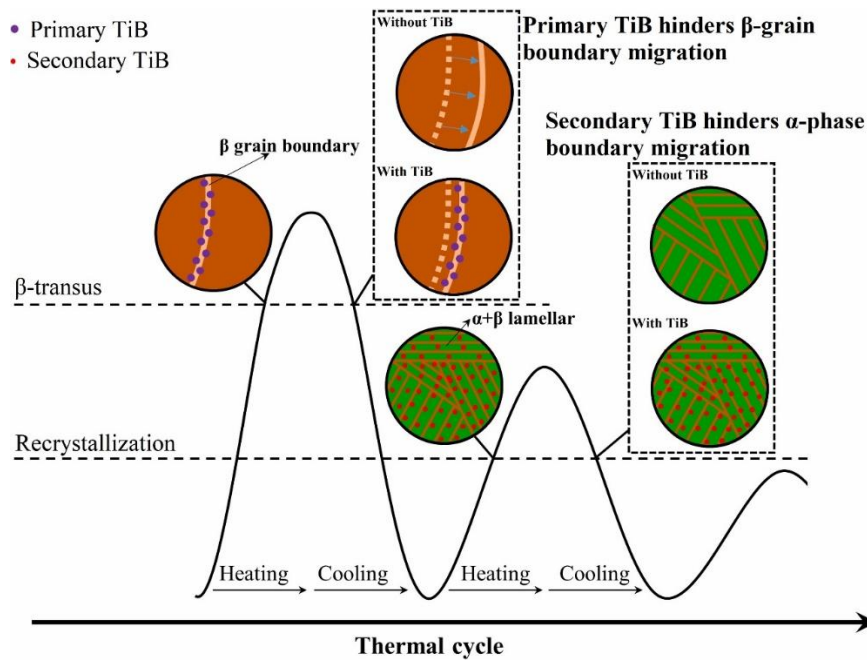


Figure 6-28 Schematic diagram of TiB-restricted grain growth during post-deposition thermal cycling.

6.9 Conclusion

This study systematically evaluated the effects of adding boron, in both crystalline and amorphous forms (0.1 wt.%), to Ti6Al4V alloys fabricated via Powder Bed Fusion–Laser Beam (PBF-LB/M). The influence of boron modification on grain refinement, densification, hardness, phase transformations, microstructural morphology, and crystallographic texture was investigated under various laser parameters (100W and 150W powers, different exposure times). The main findings are summarized as follows:

- Relative density strongly depended on laser parameters, particularly power and exposure time.
- Crystalline boron modification consistently produced the highest relative density, outperforming both amorphous boron-modified and unmodified alloys across all tested conditions, especially at higher linear energy densities (LEDs).
- Amorphous boron also improved densification compared to the unmodified alloy, though less effectively than crystalline boron, highlighting the importance of boron's crystallinity in reducing porosity.
- Density measurements via Archimedes' principle were more reliable than optical microscopy, providing a better representation of bulk properties.
- Hardness distributions significantly varied with thermal gradients induced by laser parameters. Longer exposure times generally resulted in hardness reduction in the alloy's interior due to phase transformations.

- Crystalline boron-modified Ti6Al4V showed consistently higher and more uniform hardness distributions at both 150W and 100W laser powers, markedly surpassing both amorphous boron-modified and unmodified alloys.
- At lower power (100W), alloys exhibited reduced hardness and increased variability. Amorphous boron-modified alloys were notably more sensitive to power reductions compared to crystalline boron-modified alloys, which maintained relatively stable mechanical properties.
- Boron addition, especially in crystalline form, promoted significant $\alpha' \rightarrow \alpha + \beta$ phase transformation, more prominently at higher exposure times.
- XRD analyses demonstrated crystalline boron-modified alloys had narrower diffraction peaks, higher β -phase volume fractions, and increased lattice expansion, suggesting enhanced phase transformation kinetics, particularly at lower laser power settings (100W).
- Unmodified Ti6Al4V predominantly retained martensitic α' phases, particularly at shorter exposure times.
- Both crystalline and amorphous boron significantly influenced microstructural evolution, promoting refined lamellar α/β structures accompanied by uniformly dispersed TiB particles, especially at increased exposure times.
- Crystalline boron modification exhibited greater effectiveness in stabilizing and refining $\alpha + \beta$ microstructures, resulting in superior microstructural homogeneity compared to amorphous boron.
- Boron modification dramatically refined the prior- β grain structures, significantly shifting grain morphology from elongated columnar towards equiaxed grain structures.
- Crystalline boron displayed the most pronounced grain-refining capability, particularly evident at longer exposure times, reducing grain dimensions, increasing grain boundary misorientation, and randomizing crystallographic texture more effectively than amorphous boron and unmodified alloys.
- Boron addition reduced α -variant selection, diminished the prevalence of self-accommodated Type 2 α/α variant boundaries, and led to variant boundary distributions closer to theoretical predictions.
- Alpha variants predominantly formed Category I triple- α clusters (with Type 2 α/α boundaries) in equiaxed grain structures, and Category II clusters in columnar grain structures, indicating that self-accommodation to transformation strain remains the primary mechanism influencing α -variant clustering.

Overall, crystalline boron addition proved superior to amorphous boron in achieving enhanced densification, hardness uniformity, microstructural refinement, and controlled grain morphology and texture in PBF-LB/M fabricated Ti6Al4V alloys. This demonstrates crystalline boron's effectiveness as an inoculant for tailoring advanced microstructures and mechanical properties in additive manufacturing of titanium alloys.

CHAPTER 7

MECHANICAL PROPERTIES OF BORON-MODIFIED Ti6Al4V FABRICATED BY PBF-LB/M

7.1 Microstructural Evolution

7.1.1 As-Built Condition

Since the tensile samples used in this study are relatively thin, microstructural characterization was conducted to assess whether the structure aligns with the findings presented in Chapter 6. The SEM-BSE images highlight the distinct microstructural evolution between the as-built Ti6Al4V, and boron-modified variants produced via PBF-LB/M. The as-built unmodified samples (Figure 7-1(a), (b)) exhibited a fully martensitic α' structure, typical of rapid solidification during the solidification, characterized by coarse, needle-like α' laths. However, the introduction of boron dramatically altered the microstructure. In the amorphous boron-modified Ti6Al4V (Figure 7-1(a'), (b')), a transition from a martensitic structure to an $\alpha+\beta$ phase was evident, with a finer lamellar structure replacing the coarser martensitic morphology as expected. This suggests that boron addition suppresses martensitic formation, promoting the stabilization of β -phase and leading to a more controlled $\alpha+\beta$ microstructure. The crystalline boron-modified Ti6Al4V (Figure 7-1(a''), (b'')), further enhances this refinement, displaying a much finer and more homogeneously distributed $\alpha+\beta$ lamellar structure together with TiB precipitates. The increased refinement in the crystalline boron-modified samples can be attributed to the more effective nucleation capability of crystalline boron, facilitating the formation of smaller and more equiaxed grains compared to the amorphous boron-modified samples.

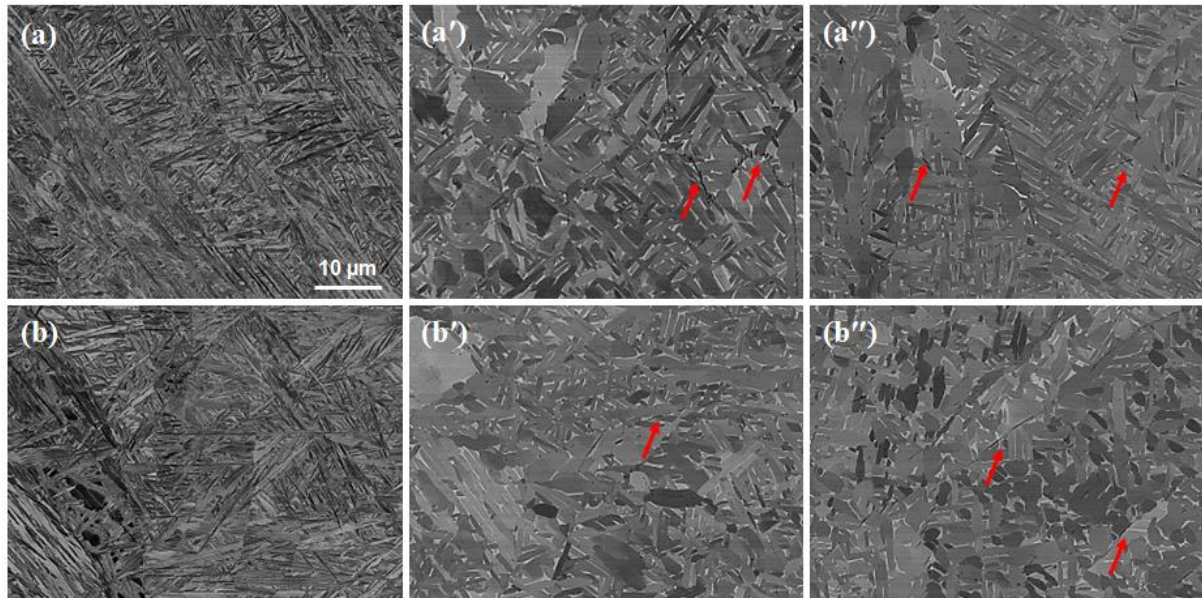


Figure 7-1 SEM-BSE images of as-built Ti6Al4V and boron-modified Ti6Al4V microstructures taken near the fractured region. (a) Longitudinal section of Ti6Al4V, and (b) Transverse section of Ti6Al4V. (a') Longitudinal section of amorphous boron-modified Ti6Al4V, and (b') Transverse section of amorphous boron-modified Ti6Al4V. (a'') Longitudinal section of crystalline boron-modified Ti6Al4V, and (b'') Transverse section of crystalline boron-modified Ti6Al4V. Red arrows indicate TiB precipitates in the alloys.

The EBSD inverse pole figure orientation maps of the reconstructed β phase in both longitudinal and transverse sections of the as-built unmodified and boron-modified Ti6Al4V alloys near the fractured regions is illustrated in Figure 7-2. In the as-built Ti6Al4V alloy (Figure 7-2(a), (b)), the β grains were large and nearly equiaxed, with distinct grain boundaries and various crystallographic orientations indicated by different colours. The grain size was relatively coarse. Additionally, there were regions of dark spots, representing porosity, which could negatively affect the mechanical integrity of the alloy, particularly under tensile loading. The distribution of grain orientations appeared random, indicating that the texture was not highly anisotropic, which may lead to more uniform mechanical properties in different loading directions. The amorphous boron-modified Ti6Al4V alloy shown in Figure 7-2(a') and (b') reveal distinct grain structures in both the Longitudinal and Transverse sections of fractured surfaces. In the longitudinal section shown in image Figure 7-2(a'), the grains are highly elongated and exhibit a strong columnar morphology aligned with the build direction. This columnar structure, while common in additively manufactured alloys due to directional solidification, contrasted with the expectations for boron-modified Ti6Al4V, where more equiaxed grains were anticipated. This discrepancy suggests that the grain refinement effect of boron was less effective in longitudinal section than initially predicted, contradicting the grain structure observations discussed in Chapter 6. In contrast, the transverse section in Figure 7-2(b') displayed the expected equiaxed grains, which align with the expected outcome of boron addition, promoting grain refinement in this plane. The presence of equiaxed grains in the

Transverse section confirms that boron still influences the microstructure, but its effect is more prominent in this orientation compared to the longitudinal section. In the longitudinal sections of crystalline boron-modified Ti6Al4V shown in Figure 7-2(a''), the grains exhibited elongated grains oriented along the build direction as seen in amorphous boron-modified case. The elongated, columnar grains in this section also indicated a deviation from the grain refinement observed in the earlier analysis. In contrast, the transverse section in Figure 7-2(b'') showed a well-refined, equiaxed grain structure, which stands in stark contrast to the longitudinal section. The grains in this plane are more uniformly distributed and lack the strong alignment seen in the longitudinal direction.

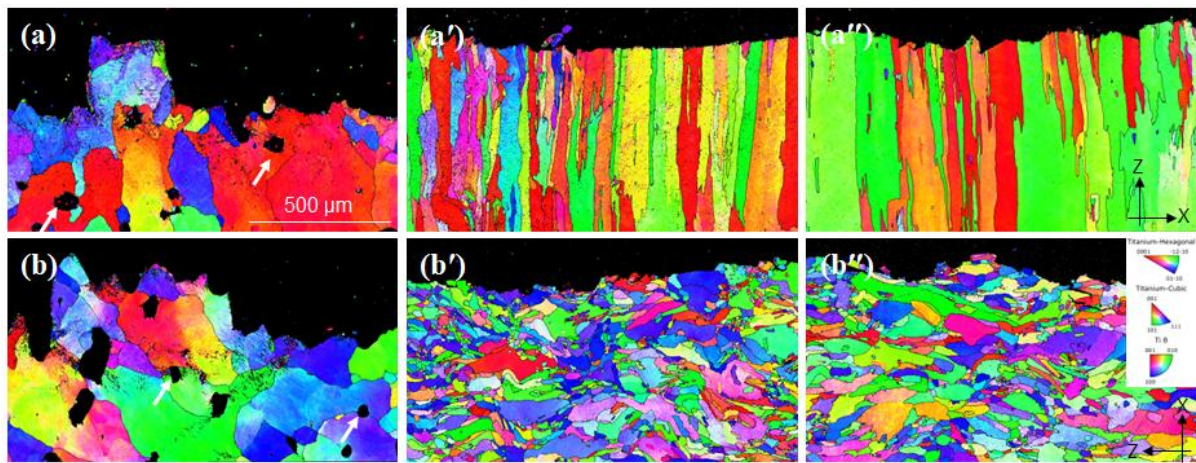


Figure 7-2 EBSD inverse pole figure orientation maps of reconstructed β phase of as-built Ti6Al4V and boron-modified Ti6Al4V microstructures taken near the fractured region. (a) Longitudinal section of Ti6Al4V, and (b) Transverse section of Ti6Al4V. (a') Longitudinal section of amorphous boron-modified Ti6Al4V, and (b') Transverse section of amorphous boron-modified Ti6Al4V. (a'') Longitudinal section of crystalline boron-modified Ti6Al4V, and (b'') Transverse section of crystalline boron-modified Ti6Al4V. White arrows indicate porosities observed in the samples.

7.1.2 Heat-Treated Condition

Figure 7-3 show the microstructures of heat-treated unmodified and boron-modified Ti6Al4V alloys near the fractured regions. After heat treatment, all alloys exhibited an $\alpha+\beta$ phase structure, which is expected due to the annealing process allowing sufficient diffusion for the stabilization of the equilibrium phases, as opposed to the martensitic structure observed in the as-built condition. In the heat-treated Ti6Al4V alloy (Figure 7-3(a), (b)), both longitudinal and transverse sections showed a coarsened $\alpha+\beta$ structure. The α phase appears as elongated laths, and β phase regions are clearly distributed between the α laths. Compared to the as-built condition, where a fine martensitic α' was dominant, the heat treatment leads to a more relaxed and coarser $\alpha+\beta$ microstructure. For the amorphous boron-modified Ti6Al4V alloy (Figure 7-3(a'), (b')), the microstructure also consisted of fine $\alpha+\beta$ phases with TiB precipitates. The α phase laths were smaller, and the β phase was more uniformly distributed. The microstructure in the as-built condition already contained $\alpha+\beta$ phases, but the heat treatment further refined

the distribution. In the crystalline boron-modified Ti6Al4V alloy (Figure 7-3(a''), (b'')), there was even more pronounced refinement of the α phase. The α laths were much finer, and the microstructure was more uniform compared to both the amorphous boron-modified and unmodified alloys. The refinement was greater in the heat-treated condition, with a better-defined $\alpha+\beta$ structure.

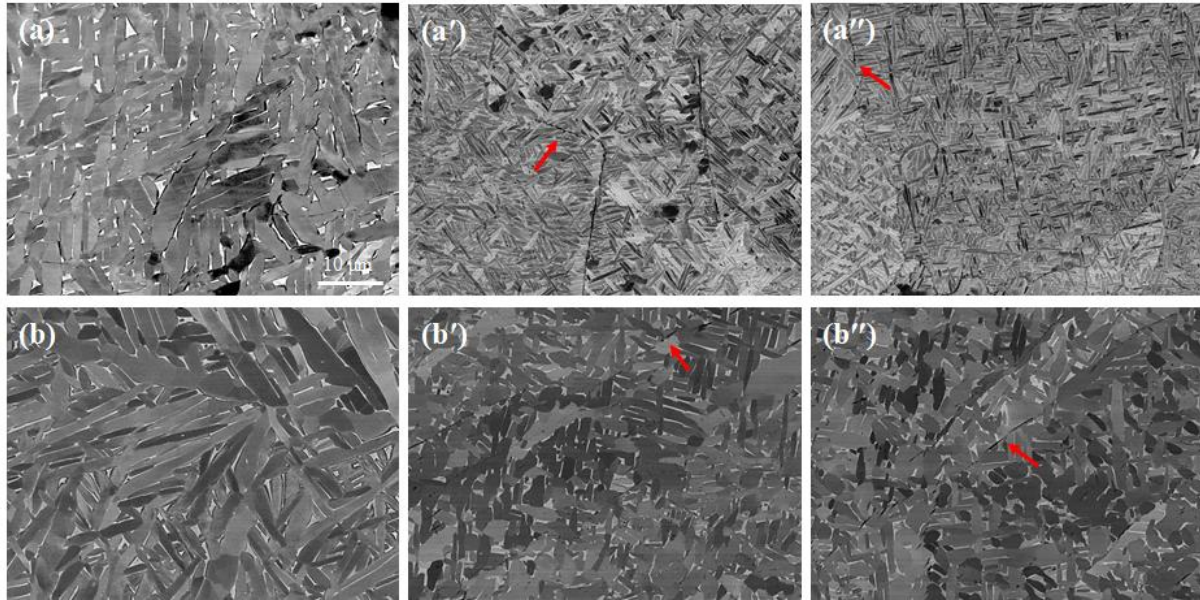


Figure 7-3 SEM-BSE images of heat-treated Ti6Al4V and boron-modified Ti6Al4V microstructures taken near the fractured region. (a) Longitudinal section of Ti6Al4V, and (b) Transverse section of Ti6Al4V. (a') Longitudinal section of amorphous boron-modified Ti6Al4V, and (b') Transverse section of amorphous boron-modified Ti6Al4V. (a'') Longitudinal section of crystalline boron-modified Ti6Al4V, and (b'') Transverse section of crystalline boron-modified Ti6Al4V. Red arrows indicate TiB precipitates in the alloys.

Figure 7-4 shows notable differences in the prior- β grain structure maps for the heat-treated samples between Longitudinal and Transverse sections for unmodified, and 0.1 wt.%B-modified Ti6Al4V alloys. In the longitudinal sections, the unmodified alloy (Figure 7-4(a)) exhibited predominantly near equiaxed grains with slight elongation along the build direction, indicating a relatively uniform grain structure post-heat treatment. However, in the amorphous and crystalline boron-modified alloys (Figure 7-4(a') and (a'')), the β grains in the longitudinal sections were mainly columnar and strongly aligned along the build direction with a few equiaxed grains. This columnar structure in the boron-modified alloys suggested despite heat treatment, the grain morphology remains elongated in the longitudinal direction, contrasting with the nearly equiaxed grains seen in the unmodified alloy. In the transverse sections, all three alloys display equiaxed grain structures. The unmodified alloy (Figure 7-4(b)) showed larger, equiaxed grains typical of a heat-treated material. Both the amorphous and crystalline boron-modified Ti6Al4V alloys (Figure 7-4(b') and (b'')) exhibited a more refined and uniform equiaxed grain structure compared to the longitudinal sections, with the crystalline boron-

modified alloy showing slightly finer grains than the amorphous variant. This indicates that boron, particularly in its crystalline form, promoted grain refinement more effectively in the Transverse plane post-heat treatment. Overall, the transverse sections consistently exhibited equiaxed grains across all alloys, while the longitudinal sections revealed a significant grain elongation in the boron-modified alloys, deviating from the expected equiaxed morphology.

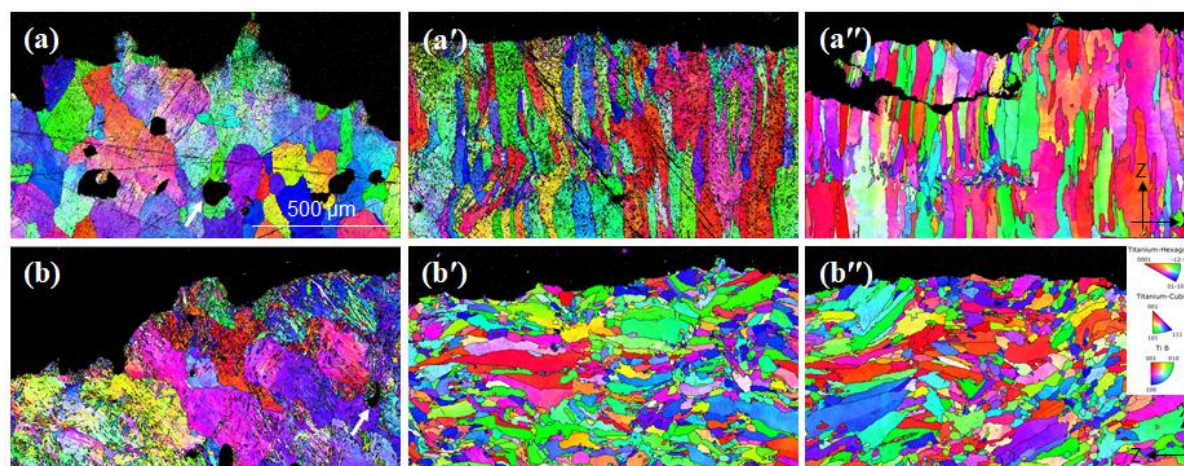


Figure 7-4 EBSD inverse pole figure orientation maps of reconstructed β phase of heat-treated Ti6Al4V and boron-modified Ti6Al4V microstructures taken near the fractured region. (a) Longitudinal section of Ti6Al4V, and (b) Transverse section of Ti6Al4V. (a') Longitudinal section of amorphous boron-modified Ti6Al4V, and (b') Transverse section of amorphous boron-modified Ti6Al4V. (a'') Longitudinal section of crystalline boron-modified Ti6Al4V, and (b'') Transverse section of crystalline boron-modified Ti6Al4V. White arrows indicate porosities observed in the samples.

7.2 Tensile Property and Anisotropy of As-Built Samples

The room temperature tensile properties of PBF-LB/M produced Ti6Al4V and Ti6Al4V-0.1B alloys were tested along the longitudinal and transverse directions in the as-built condition (Figure 7-5(a) and (b)). The results demonstrate that the mechanical performance of base alloy was significantly influenced by boron addition and build orientation. The minimum ASTM requirements for ultimate tensile strength, yield strength and elongation for forged Ti6Al4V is 895MPa, 825MPa and 8%, respectively. For unmodified alloy, the average tensile and yield strength values were 1139MPa and 1017MPa, respectively, when the load direction was parallel to the build direction, and 1155 MPa and 1032 MPa when the load direction was perpendicular to the build direction. While these values met the strength requirements, the elongation was significantly below ASTM standards, particularly when the load was parallel to the build direction (2.78%) due to the presence of martensitic α' and porosity. Compared to the unmodified alloy, the addition of amorphous boron caused a substantial improvement in both tensile and yield strength. When the load direction was parallel to the build direction, tensile strength increased by approximately 9.5% to 1248MPa, while yield strength rose by 2.3% to 1040MPa. When the load direction was perpendicular to the build direction, tensile strength

increased by 20.9% to 1397MPa, and yield strength increased by 12.3% to 1159 MPa. The elongation in both orientations also improved significantly, with values of 8.87% (longitudinal) and 9.52% (perpendicular), indicating that the addition of amorphous boron refines the microstructure and enhanced ductility. The crystalline boron-modified alloy exhibited the most pronounced increase in tensile properties. When the load direction was parallel to the build direction, tensile strength increased by 10.5% to 1259MPa, and yield strength increased by 10.4% to 1123MPa compared to the unmodified alloy. When the load direction was perpendicular to the build direction, tensile strength rose by 27% to 1467MPa, while yield strength increased by 32.5% to 1367MPa. Elongation also showed a marked improvement, with values of 11.25% (longitudinal) and 11.82% (perpendicular). Although the boron-modified samples showed enhanced strength, mechanical anisotropy was evident, especially in the crystalline alloy, where tensile and yield strength anisotropy was predominant in the boron-modified samples (Figure 7-5(c)). While the unmodified alloy exhibited low strength anisotropy with moderate elongation anisotropy, the amorphous boron-modified samples saw a rise in tensile strength anisotropy to ~11% and yield strength anisotropy to ~10%, with moderate elongation anisotropy at ~7%. The crystalline boron-modified samples, however, had the highest tensile and yield strength anisotropy values of ~14% and ~18%, respectively, though elongation anisotropy decreased to ~5%. The mechanical anisotropy was mainly attributed to the presence of columnar grains where the elongated grain boundaries may act as stress concentrators and limit plastic deformation along the loading direction.

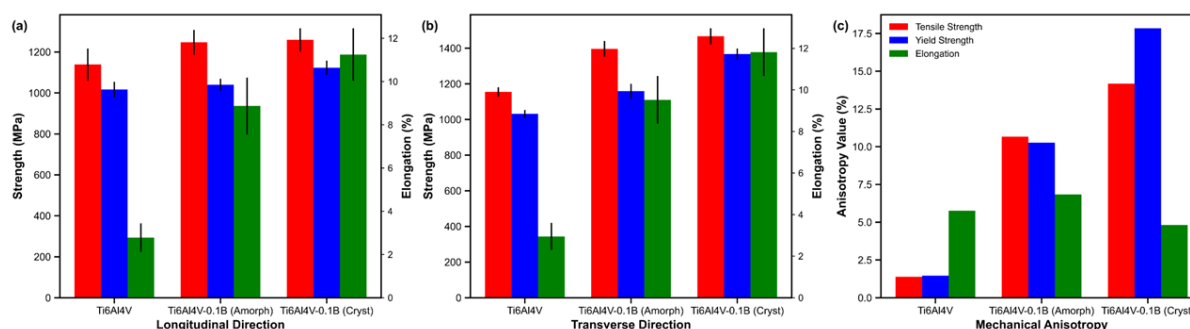


Figure 7-5 The room-temperature tensile properties of unmodified and 0.1 wt.%B-modified Ti6Al4V alloy as-built samples in (a) longitudinal direction, (b) transverse direction, and (c) mechanical anisotropy, comparing tensile strength, yield strength, and elongation across all samples.

The fracture surface analysis of the sample produced by unmodified alloy revealed features consistent with brittle failure mechanisms. In Figure 7-6(a), the low magnification image highlighted the macroscale fracture surface, characterized by planar, faceted regions indicative of limited plastic deformation. The presence of gas porosity was also evident, which may have acted as stress concentrators, contributing to crack initiation and propagation under applied stress. At higher magnification (Figure 7-6(b)), the detailed view of the facets showed a dominant cleavage-type fracture, confirming a brittle fracture mode. The sharp and flat fracture facets, along with the absence of ductile dimples, further supported the conclusion that the

sample fractured with minimal energy absorption, typical of brittle materials. These observations suggest that the material's fracture behaviour is controlled primarily by crack propagation along cleavage planes, consistent with rapid fracture under stress without significant plastic deformation. For the amorphous boron-modified alloy (Figure 7-6(a') and (b')) the low magnification image (Figure 7-6(a')) showed a rough fracture surface, consistent with ductile fracture. At higher magnification (Figure 7-6(b')), the presence of numerous dimples and microvoids, indicated by the arrows, confirmed a ductile fracture mode, characterized by extensive plastic deformation. For the crystalline boron-modified alloy, the low magnification image (Figure 7-6(a'')) revealed characteristics of brittle fracture. The smooth, planar facets and radial crack propagation patterns, arising from a point of initiation, were indicative of a rapid and catastrophic brittle failure. At higher magnification (Figure 7-6(b'')), the fracture surface showed a more ductile mode. The presence of dimples and microvoid coalescence points to localized plastic deformation prior to final failure. These features were characteristic of ductile fracture, where the material absorbed more energy and exhibited plastic deformation before breaking. The rough and irregular surface, along with the extensive dimples, contrasted with the smooth brittle facets observed in the macrograph. This suggests that while the material initially failed in a brittle manner, there were regions where plastic deformation occurred before final failure.

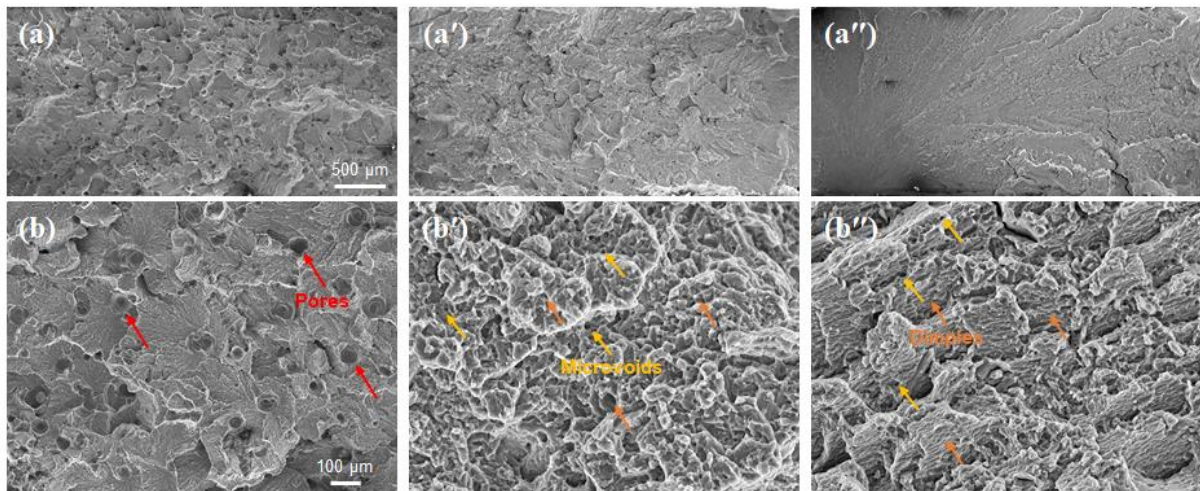


Figure 7-6 SEM-SE images of fracture surfaces of as-built samples produced Longitudinally from unmodified and boron-modified Ti6Al4V alloys. Images (a) and (b) show unmodified Ti6Al4V. Images (a') and (b') display amorphous boron-modified Ti6Al4V, while (a'') and (b'') depict crystalline boron-modified Ti6Al4V.

The fracture surface analysis of Transversely as-built Ti6Al4V samples reveals distinct differences between the unmodified and boron-modified alloys, as shown in Figure 7-7. For the unmodified alloy, the fracture surface imaged by low magnification (Figure 7-7(a)) was dominated by visible pores, which could act as stress concentrators and contribute to crack initiation. The higher magnification image (Figure 7-7(b)) showed a combination of dimpled

and flat regions, indicative of a mixed fracture mode, with the dimples suggesting localized plastic deformation prior to failure. In the amorphous boron-modified alloy, the fracture surface at low magnification (Figure 7-7(a')) was dominated by large, flat, and faceted regions with visible striations or cleavage-like planes. These features suggested the crack propagated rapidly through the material with little to no plastic deformation, which is typical of brittle failure. However, when examined at higher magnification (Figure 7-7(b')), the fracture surface revealed a different aspect. The presence of dimples and microvoid coalescence indicates that, on a finer scale, the material experienced localized ductile deformation before failure. These dimples suggest while the overall fracture may appear brittle, there were regions where the material absorbed some energy and underwent plastic deformation. For the crystalline boron-modified alloy, the fracture surface at low magnification (Figure 7-7(a'')) appeared smooth and wavy, with no distinct cleavage planes or sharp, flat facets typically associated with brittle failure. The absence of any clear striations or facets reinforces the conclusion that the material failed in a ductile manner, where the crack propagated more slowly and plastically deformed the surrounding areas before complete failure. The fracture surface shown in this high-magnification image (Figure 7-7(b'')) revealed typical features of ductile fracture. The surface was highly irregular, with a noticeable presence of dimples formed by microvoid coalescence. These dimples, characteristic of plastic deformation, indicate that the material underwent localized deformation as microvoids formed, grew, and eventually coalesced to lead to final failure.

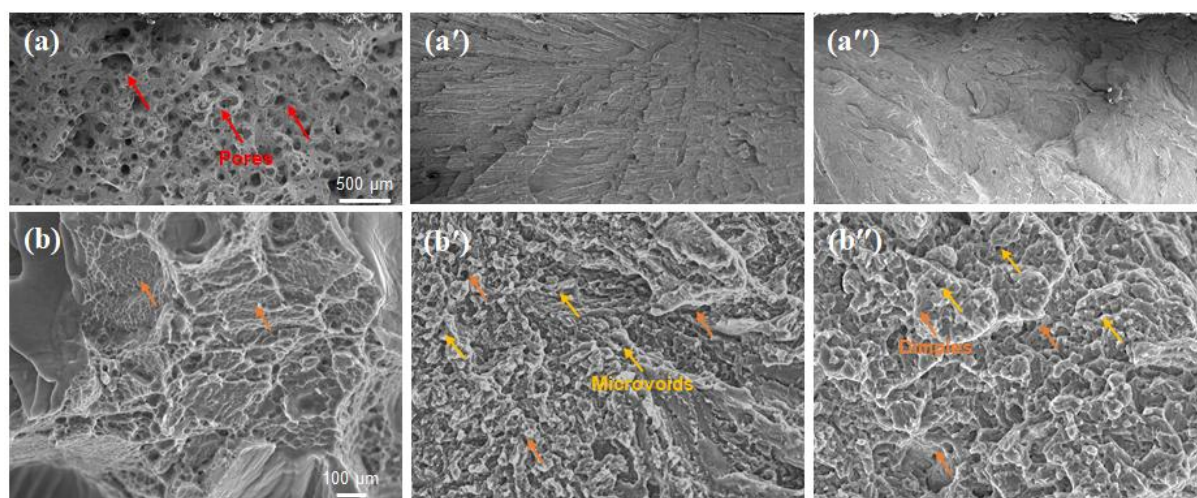


Figure 7-7 SEM-SE images of fracture surfaces of as-built samples produced Transversely from unmodified and boron-modified Ti6Al4V alloys. Images (a) and (b) show unmodified Ti6Al4V. Images (a') and (b') display amorphous boron-modified Ti6Al4V, while (a'') and (b'') depict crystalline boron-modified Ti6Al4V.

7.3 Tensile Property and Anisotropy of Heat-Treated Samples

The room temperature tensile properties of heat-treated, transversely produced unmodified and 0.1 wt.%B-modified Ti6Al4V alloys were evaluated along the longitudinal and transverse

directions (Figure 7-8(a) and (b)). The results show that both the boron addition and heat treatment significantly influenced the mechanical properties. For the unmodified alloy, the average tensile strength in the longitudinal direction was 1058MPa, and the yield strength was 954MPa, with an elongation of 5.47%. In the transverse direction, the tensile strength slightly decreased to 1045MPa, while the yield strength was 965MPa, with an elongation of 5.05%. These values are slightly below typical standards but indicate a balance between strength and ductility. The amorphous boron-modified alloy demonstrated improved mechanical properties compared to the unmodified alloy. In the longitudinal direction, the tensile strength increased to 1235MPa, and the yield strength rose to 1056MPa. The transverse direction showed a further increase in tensile strength to 1259MPa, and yield strength to 1120MPa. The elongation also improved significantly, with values of 13.42% in the longitudinal direction and 15.47% in the transverse direction. The crystalline boron-modified alloy exhibited the highest strength values. In the longitudinal direction, the tensile strength increased to 1256 MPa, and the yield strength rose to 1146MPa. In the transverse direction, the tensile strength reached 1312MPa, while yield strength increased to 1197MPa. Elongation was also significantly higher, with values of 14.37% in the longitudinal direction and 17.22% in the transverse direction. Mechanical anisotropy was also observed in all samples (Figure 7-8(c)). The unmodified alloy exhibited relatively low anisotropy, with ultimate tensile strength anisotropy at ~1.24% and elongation anisotropy at ~8.32%. The amorphous boron-modified alloy exhibited an increase in strength anisotropy to ~1.91% and elongation anisotropy to ~13.25%. The crystalline boron-modified alloy displayed the highest strength anisotropy at ~4.27% and elongation anisotropy at ~16.55%. These differences in anisotropy were likely attributed to the microstructural variations induced by the boron addition, where the presence of columnar grains may restrict plastic deformation and influence the material's anisotropy in mechanical behaviour.

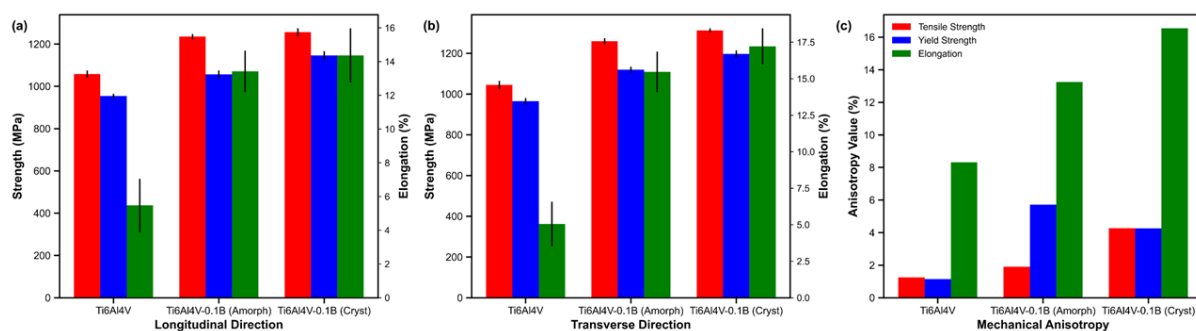


Figure 7-8 The room-temperature tensile properties of unmodified and 0.1 wt.%B-modified Ti6Al4V alloy heat-treated samples in (a) longitudinal direction, (b) transverse direction, and (c) mechanical anisotropy, comparing tensile strength, yield strength, and elongation across all samples.

The fracture surface analysis of heat-treated, longitudinally produced samples shown in Figure 7-9 shows distinct differences in ductility and brittleness between unmodified and boron-modified Ti6Al4V alloys. The fracture surface analysis of the unmodified alloy sample revealed a combination of surface features indicative of a mixed-mode fracture. In the low magnification

image (Figure 7-9(a)), the fracture surface appeared rough and uneven, with a variety of surface features and gas pores. However, the overall surface morphology was relatively smooth in certain areas, indicating brittle fracture could have played a role in the failure, with rapid crack propagation through parts of the material. The high magnification image (Figure 7-9(b)) provided a more detailed view, showing a rough texture with the presence of dimples and tear ridges, characteristic of ductile fracture. These dimples suggested the material underwent localized plastic deformation before failure, confirming that the material absorbed some energy during the fracture process. However, the surface also contained some flat regions, indicative of brittle fracture characteristics in certain areas. The fracture surface analysis of the amorphous boron-modified alloy sample, based on the fracture surfaces, pointed towards a ductile fracture mechanism. In the low magnification image (Figure 7-9(a')), the surface showed a characteristic uneven and rough texture of a ductile fracture. There were no clear planar facets or flat regions typically seen in brittle fractures, indicating that the material did not fail in a sudden, brittle manner. The high magnification image (Figure 7-9(b')) revealed a dimpled surface formed due to microvoid coalescence, a common ductile failure mechanism. The densely packed dimples indicated the material underwent substantial plastic deformation before failure, absorbing significant energy as the microvoids formed, grew, and coalesced. The fracture surface analysis of crystalline boron-modified alloy sample revealed a combination of brittle and ductile fracture characteristics. In the low magnification image (Figure 7-9(a'')), the surface showed a mixture of layered, planar regions and rough, uneven textures. The layered regions suggest rapid crack propagation with minimal plastic deformation, while the rougher sections in the image display more irregular features, pointing towards ductile behaviour. When examined with the high magnification image (Figure 7-9(b'')), a more detailed view revealed a rough surface with clear dimples and microvoid coalescence as long as intergranular fracture.

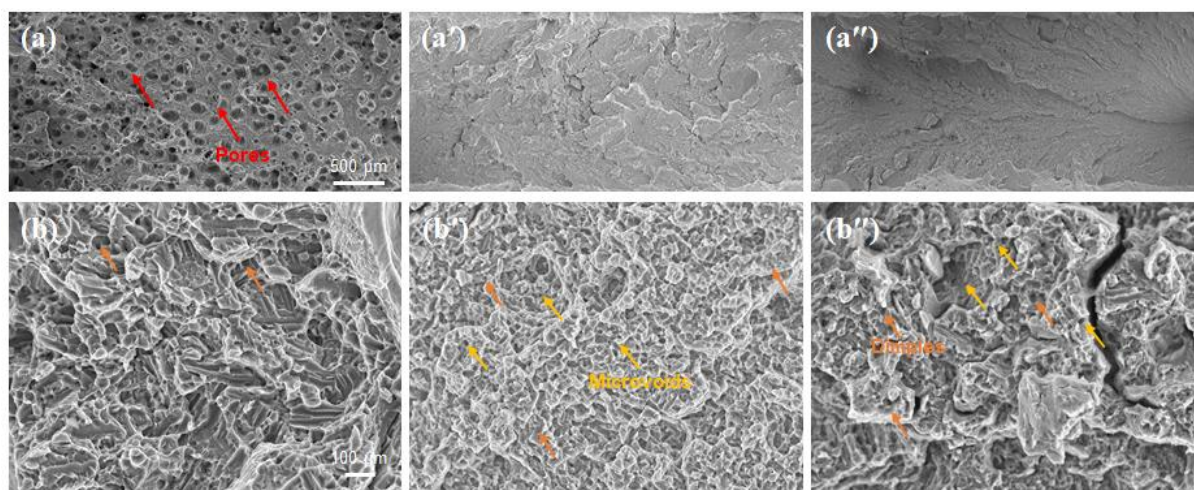


Figure 7-9 SEM-SE images of fracture surfaces of heat-treated samples produced Longitudinally from unmodified and boron-modified Ti6Al4V alloys. Images (a) and (b) show unmodified Ti6Al4V. Images (a') and (b') display amorphous boron-modified Ti6Al4V, while (a'') and (b'') depict crystalline boron-modified Ti6Al4V.

Figure 7-10 shows the fracture surfaces of heat-treated samples, produced transversely from unmodified and boron-modified Ti6Al4V alloys. For the unmodified alloy, the low magnification image (Figure 7-10(a)) revealed a rough surface with visible pores, which could act as stress concentrators, while the high magnification image (Figure 7-10(b)) showed dimpled regions, indicating ductile fracture through microvoid coalescence. In the case of the amorphous boron-modified alloy, the low magnification image (Figure 7-10(a')) showed a relatively smooth surface with fewer irregularities, suggesting less brittle behaviour. Upon closer examination with the high magnification image (Figure 7-10(b')), numerous microvoids and dimples became evident, further supporting a ductile fracture mechanism. For the crystalline boron-modified alloy, the low magnification image (Figure 7-10(a'')) revealed planar, layered regions, suggesting a brittle fracture. However, when viewed under higher magnification (Figure 7-10(b'')), a more complex fracture surface emerges. The high magnification image showed a clear distinction between brittle regions and ductile regions. The brittle areas displayed flat facets, while the ductile areas contained dimples and microvoids, confirming localized plastic deformation. This mixed fracture mode indicates that while brittle failure dominated certain regions, ductile behaviour still played a role in other areas.

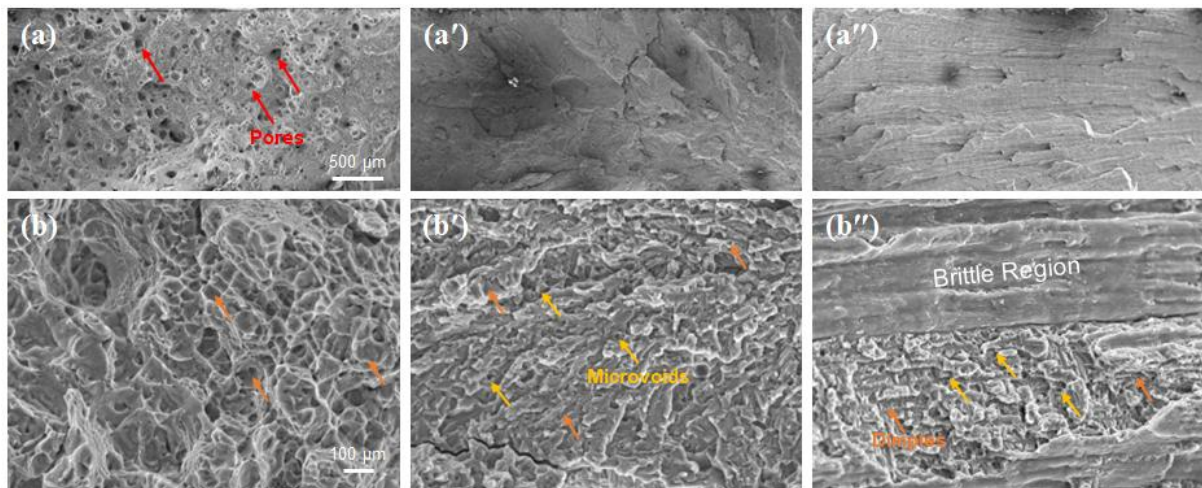


Figure 7-10 SEM-SE images of fracture surfaces of heat-treated samples produced Transversely from unmodified and boron-modified Ti6Al4V alloys. Images (a) and (b) show unmodified Ti6Al4V. Images (a') and (b') display amorphous boron-modified Ti6Al4V, while (a'') and (b'') depict crystalline boron-modified Ti6Al4V.

7.4 Discussion

7.4.1 The Analysis of Schmid Factors and Slip System

The distribution of Schmid Factors (SFs) for all slip and twinning systems is widely recognized as a means to evaluate material strength and deformation behaviour (Dharmendra et al., 2020; X. Liu et al., 2020). At room temperature, the critical resolved shear stress (CRSS) ratios for the basal slip, prismatic slip, pyramidal $\langle a \rangle$ slip, pyramidal $\langle a+c \rangle$ slip, and T1 tensile twinning are reported to be 1:0.81:19:35:74, respectively (H. Li et al., 2013). Given this significant

difference in CRSS, only the basal and prismatic slip systems were considered in this study. The calculation process involved two main steps: the SFs were determined for all six variants within each slip system. Then, using the formula $\sigma_s = \tau_c/m$ (where τ_c represents the normalized CRSS, m is the SF, and σ_s is the yield strength expressed as a ratio rather than an absolute value), the most likely slip system to activate based on these calculations was identified. This analysis was carried out using AztecCrystal software, which allowed efficient processing of the large pixel data sets collected.

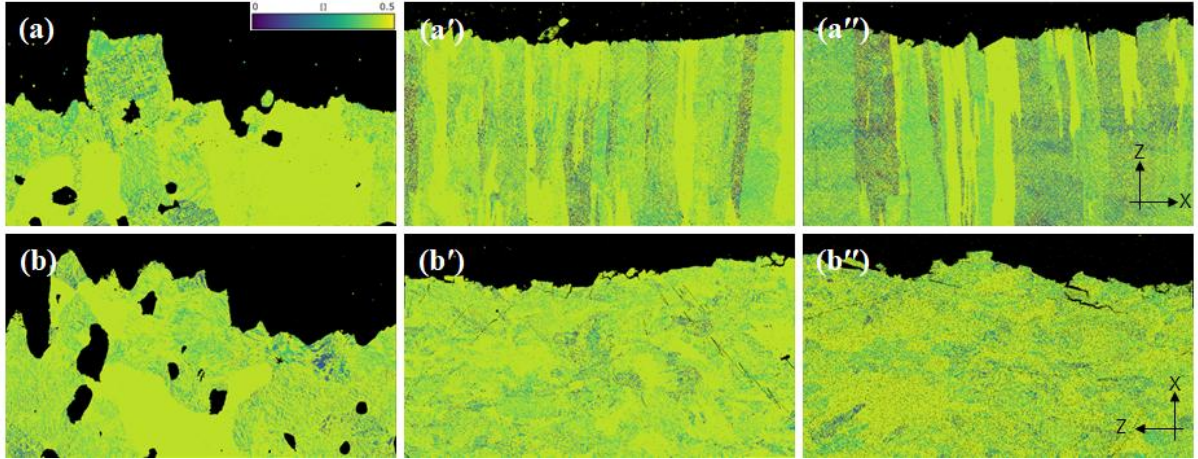


Figure 7-11 The distribution of Schmid Factors of as-built unmodified and boron-modified Ti6Al4V. The Schmid factor maps of (a) and (b) Ti6Al4V; (a') and (b') amorphous boron-modified Ti6Al4V; (a'') and (b'') crystalline boron-modified Ti6Al4V. Top SF maps show longitudinal sections, and bottom SF maps show transverse sections.

Figure 7-11 presents the overall SF distribution of as-built unmodified and boron-modified Ti6Al4V, and the statistical results of the $\overline{SF}$ is listed in Table 7-1. The area represents the proportion of the grains likely to activate basal (or prismatic) slip relative to the total area in the IPF map. The $\overline{SF}$ refers to the mean Schmid Factor determined using an area-weighted algorithm. Additionally, considering the critical resolved shear stress (CRSS) ratio between basal and prismatic slip systems (1:0.81), the average yield stresses ($\overline{YS}$) were estimated accordingly. The results indicated that the yield strength was at a relatively poor level when loaded longitudinally. The trend was clear that as the loading direction changed from transverse ($\theta=0^\circ$) to longitudinal direction ($\theta=90^\circ$), the $\overline{SF}$ values increased and thus the $\overline{YS}$ values decreased. In addition, for the unmodified alloy, the differences in the average value of $\overline{SF}$ ($\Delta\overline{SF}$) and $\overline{YS}$ ($\Delta\overline{YS}$) between $\theta=90^\circ$ and $\theta=0^\circ$ were 0.0024 and 0.0114, respectively. In comparison, these differences increased to 0.0139 and 0.0679 for the amorphous boron-modified alloy, and 0.0149 and 0.0747 for the crystalline boron-modified alloy. This suggests that the transition from columnar to equiaxed grains can significantly reduce strength anisotropy in the material.

Table 7-1 The calculation results of the Schmid Factors of as-built unmodified and boron-modified Ti6Al4V.

Sample	Loading Direction	Basal slip $\{0001\}\langle 11\bar{2}0 \rangle$			Prismatic slip $\{10\bar{1}0\}\langle 11\bar{2}0 \rangle$		
		Area	$\overline{SF}$	$\overline{YS}$	Area	$\overline{SF}$	$\overline{YS}$
Ti6Al4V	90°	56.69	0.4595	2.1763	29.73	0.4587	1.7659
	0°	40.00	0.4571	2.1877	42.27	0.4565	1.7744
Ti6Al4V-0.1B (Amorph)	90°	43.78	0.4595	2.1763	32.02	0.4503	1.7988
	0°	40.77	0.4456	2.2442	40.10	0.4332	1.8698
Ti6Al4V-0.1B (Cryst)	90°	42.11	0.4542	2.2017	38.72	0.4557	1.7775
	0°	35.15	0.4393	2.2763	27.79	0.4428	1.8293

In the initial stage of the heat treatment process, a holding temperature of 925°C was selected, which is below the β -transus temperature ($\sim 990^\circ\text{C}$) and, therefore, did not fully eliminate the primary β structure of the alloy. However, 925°C is still within the high-temperature solid solution range, where the β -phase constitutes more than 50% of the molar ratio under equilibrium conditions, as indicated by the phase diagram (Ter Haar & Becker, 2018; S. Zhang et al., 2009). Any martensitic α' formed during the PBF-LB/M process would have decomposed during the subsequent aging step at 700°C. This heat treatment led to coarsening of the prior β grains and an increase in the thickness of the α laths. The SF maps shown in Figure 7-12 demonstrate that the heat treatment did not significantly alter the orientation relationship between adjacent laths, indicating no substantial recrystallization occurred. The statistical results of the $\overline{SF}$ and $\overline{YS}$, listed in Table 7-2, revealed only slight variations at longitudinal and transverse direction with a similar trend to the as-deposited sample.

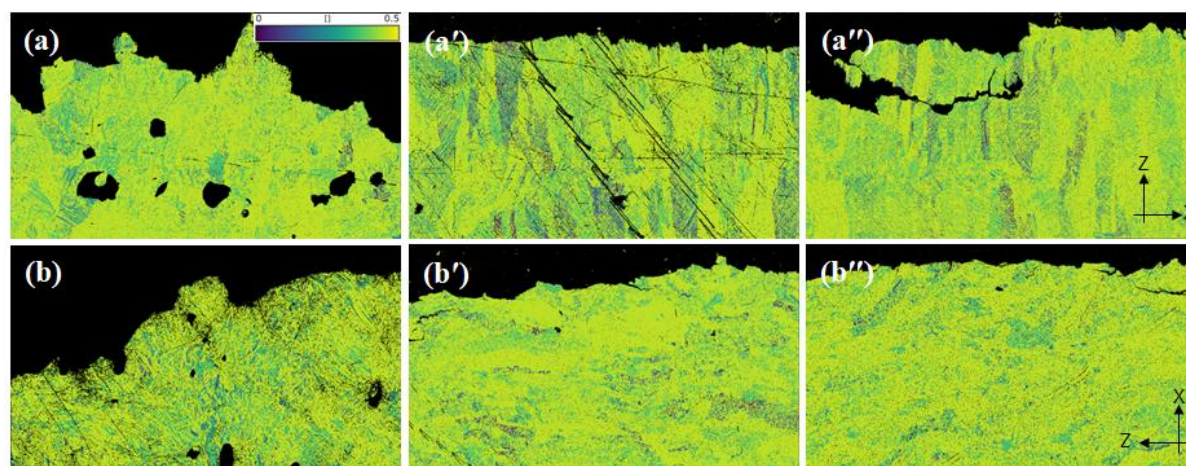


Figure 7-12 The distribution of Schmid Factors of heat-treated Ti6Al4V and boron-modified Ti6Al4. The Schmid factor maps of (a) and (b) Ti6Al4V; (a') and (b') amorphous boron-modified Ti6Al4V; (a'') and (b'') crystalline boron-modified Ti6Al4V. Top SF maps show longitudinal sections, and bottom SF maps show transverse sections.

Table 7-2 The calculation results of the Schmid Factors of heat-treated unmodified and boron-modified Ti6Al4V.

Sample	Loading Direction	Basal slip $\{0001\}\langle 11\bar{2}0 \rangle$			Prismatic slip $\{10\bar{1}0\}\langle 11\bar{2}0 \rangle$		
		Area	$\overline{SF}$	$\overline{YS}$	Area	$\overline{SF}$	$\overline{YS}$
Ti6Al4V	90°	41.33	0.4541	2.2021	37.71	0.4501	1.7998
	0°	30.32	0.4527	2.2088	48.87	0.4457	1.8174
Ti6Al4V-0.1B (Amorph)	90°	43.98	0.4514	2.2155	28.32	0.4534	1.7865
	0°	46.13	0.4323	2.3133	33.67	0.4420	1.8327
Ti6Al4V-0.1B (Cryst)	90°	43.72	0.4487	2.2286	34.05	0.4507	1.7973
	0°	38.28	0.4238	2.3595	44.44	0.4343	1.8650

7.4.2 The relationship between the $\overline{SF}$ evolution and the Anisotropy of Strength

The results from Tables 7-1 and 7-2 show a clear pattern: as the angle of the loading direction increases, the average $\overline{SF}$ also increases, leading to a reduction in the average $\overline{YS}$. This suggests that the material strength improves when loaded in the transverse direction. As discussed in Sections 7.1 and 7.2, previous studies have often shown that horizontally oriented tensile tests on PBF-LB/M samples typically outperform longitudinal tests in terms of both strength and ductility, or at least one of these properties tends to be superior. The Schmid factor analysis in Table 7-1 and Table 7-2 was consistent with these earlier findings and helped explain the underlying mechanism behind the changes in yield strength. Moreover, the samples exhibited a strong $\langle 010 \rangle_{\text{TiB}}$ and $\langle 100 \rangle_{\beta}$ texture in their columnar microstructures. When loaded in the transverse direction, TiB whiskers that were perpendicular to the loading direction were less capable of bearing the load due to their limited contact area with the matrix. In contrast, TiB whiskers aligned parallel to the loading direction facilitated more efficient load transfer when the sample was loaded longitudinally. This contributed to increased strength at longitudinal direction and helped reduce the anisotropy caused by the dominant $\langle 100 \rangle_{\beta}$ texture. However, the results of this study revealed an unexpected trend: the tensile strength decreased as the loading direction changed from transverse to longitudinal, which contradicts what is typically observed. Two potential explanations can be suggested for this behaviour. Firstly, the number of deposition layers varied among the samples. Vertically built samples had the most deposition layers, while the horizontally built samples had fewer. This difference likely led to higher residual stresses in the vertically built samples, as a greater number of deposition layers generally results in stronger residual stresses (Y. Liu et al., 2016; Mercelis & Kruth, 2006). Secondly, residual stress-induced sample curling was most prominent in the horizontally built samples and became less severe as the angle approached vertical. The vertically built samples showed no evidence of curling, suggesting that residual stress was partially relieved. As a result, the horizontally built samples had the least residual stress due to fewer deposition layers and greater stress relief. Previous studies have shown that residual stress relief could cause a strength variation of 64–134 MPa (Simonelli et al., 2014), which aligns with the UTS variations observed in this study. Moreover, the horizontally built samples displayed equiaxed grains in their microstructure, in contrast to the columnar grains observed in the vertically built samples.

The presence of equiaxed grains is known to improve mechanical properties, such as strength and ductility, due to more uniform grain orientations and reduced anisotropy. This grain morphology, combined with the reduced residual stress, likely contributed to the enhanced mechanical performance observed in the horizontally built samples.

7.4.3 Strengthening mechanism

The boron-modified alloys demonstrated a notable increase in yield strength (σ_{YS}) compared to their unmodified counterparts ($\sigma_{YS,m}$), as detailed in Sections 7.1 and 7.2. Here, horizontally as-built crystalline boron-modified alloys were chosen to analyse the strengthening mechanisms due to its good combination of strength and ductility. Specifically, the yield strength of the boron-modified alloy, averaging 1363MPa across both 0° and 90° orientations, exceeded that of Ti6Al4V (1147MPa) by 216 MPa. This improvement in σ_{YS} can be attributed to a combination of strengthening mechanisms: the Hall-Petch effect ($\Delta\sigma_{HP}$), load-bearing contributions from TiB ($\Delta\sigma_{TiB}$), and dislocation strengthening ($\Delta\sigma_{dis}$). Given the low solid solubility of boron in the titanium matrix, the impact of boron as an interstitial solid solution can be considered negligible. Thus, when accounting for these mechanisms, the yield strength of the boron-modified alloy can be represented as follows(Y. Hu, Cong, et al., 2018b):

$$\sigma_{YS} = \Delta\sigma_{YS,m} \left(1 + \frac{\Delta\sigma_{HP}}{\Delta\sigma_{YS,m}} \right) \left(1 + \frac{\Delta\sigma_{TiB}}{\Delta\sigma_{YS,m}} \right) \left(1 + \frac{\Delta\sigma_{dis}}{\Delta\sigma_{YS,m}} \right) \quad 7.1$$

7.4.3.1 Hall-Patch Strengthening

The addition of boron resulted in a noticeable refinement of the grain structure compared to the Ti6Al4V alloy. This grain refinement contributes to an increase in yield strength, which can be quantified using the following relationship(Hansen, 2004):

$$\Delta\sigma_{HP} = k_{HP} \left(\frac{1}{\sqrt{d_2}} - \frac{1}{\sqrt{d_1}} \right) \quad 7.2$$

where d_1 and d_2 represent the grain size for unmodified and the boron-modified Ti6Al4V alloy, respectively. A detailed summary of these values is provided in Table 7-3.

Table 7-3 The contribution of strengthening mechanisms to the yield strength of boron-modified alloy.

Parameters	Value
$K_H (MPa \times \mu m)^{1/2}$	328
$d_1 (\mu m)$	255.02
$d_2 (\mu m)$	16.93
$V_f (vol\%)$	0.535
l/d	~ 21.63
C_0	0.125
$G_m (GPa)$	45
$\gamma (\mu m)$	2.5
ε_m	7.5×10^{-3}
$b_m (nm)$	0.295
$D_{TiB} (\mu m)$	1.48
$\Delta\alpha (K^{-1})$	1.25×10^{-6}
$\Delta T (^\circ C)$	~ 1300

7.4.3.2 Load-bearing Strengthening

The strong interface between α -titanium and TiB plays a key role in effectively transferring the applied load, thereby enhancing the strength of the boron-modified alloy. Additionally, the TiB whiskers contribute to the increase in yield strength (σ_{YS}) by serving as load-bearing sites during deformation. The contribution of this mechanism has been estimated as follows (X. Guo et al., 2012):

$$\Delta\sigma_{TiB} = \sigma_{YS,m} 0.5V_f \frac{l}{d} C_0 \quad 7.3$$

The parameters V_f , l , and d represent the volume fraction, length, and diameter of TiB needles, respectively, while C_0 refers to the orientation factor, ranging between 0 and 1. The specific values for these parameters are provided in Table 7-3.

7.4.3.3 Dislocation Strengthening

The increase in yield strength (σ_y) due to dislocations is typically explained by three key mechanisms: Orowan strengthening ($\Delta\sigma_{oro}$), thermal mismatch ($\Delta\sigma_{the}$), and geometrically necessary dislocations ($\Delta\sigma_{geo}$). In boron-modified alloys, nano-sized TiB particles act as obstacles to dislocation movement, contributing to Orowan strengthening. Additionally, both thermal mismatch and geometrically necessary dislocations are closely linked to the interaction between TiB whiskers and the titanium matrix, as depicted in Figure 7-13. The figure illustrates significant lattice distortion possibly near TiB whiskers, present in both the columnar and equiaxed regions of the boron-modified alloys. For boron-modified alloys produced using conventional methods with slower cooling rates, dislocation strengthening is often considered minimal or even negligible, likely due to the similar thermal expansion coefficients of TiB whiskers and the titanium matrix (G. Singh & Ramamurty, 2020). However, the rapid solidification associated with the PBF-LB/M process enhances the thermal mismatch between

TiB and the titanium matrix, leading to pronounced lattice distortion at the TiB/Ti interface (M. Fang et al., 2021c). This distortion contributes to a noticeable strengthening effect.

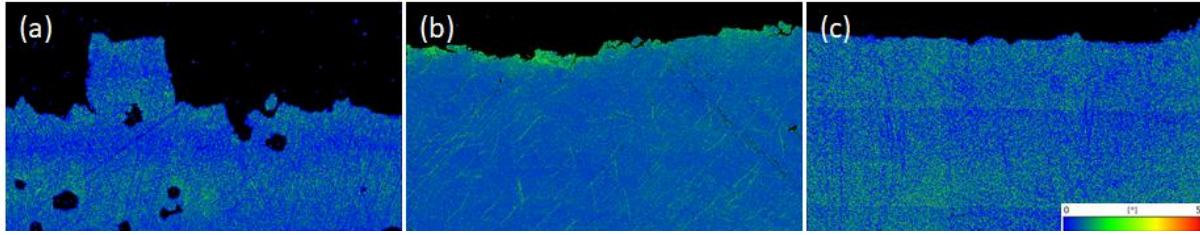


Figure 7-13 The Kernel Average Misorientation (KAM) maps of the (a) Ti6Al4V; (b) amorphous boron-modified; and (c) crystalline boron-modified Ti6Al4V alloys produced horizontally.

It has been reported that dislocation motion is effectively hindered by TiB whiskers, resulting in dislocation pileups near the TiB/Ti interface, which significantly increases the dislocation density. Dislocation accumulation around the TiB whiskers further intensifies this effect. Stress concentration tends to develop at the ends and middle regions of the whiskers, which in turn initiates microvoid formation, leading to fracture in titanium matrix composites (TMC). Based on this mechanism, the strengthening contribution from dislocations ($\Delta\sigma_{dis}$) can be quantified as described in previous studies (Brown & Stobbs, 1976; Xiao et al., 2021).

$$\Delta\sigma_{dis} = \sqrt{(\Delta\sigma_{oro})^2 + (\Delta\sigma_{the})^2 + (\Delta\sigma_{geo})^2} \quad 7.4$$

$$\Delta\sigma_{oro} = \frac{0.13G_m b_m}{\gamma} \ln \frac{D_{TiB}}{2b_m} \quad 7.5$$

$$\Delta\sigma_{geo} = 0.4G_m \sqrt{\frac{\varepsilon_m b_m V_{TiB}}{D_{TiB}}} \quad 7.6$$

$$\Delta\sigma_{the} = k G_m b_m \sqrt{12 \frac{\Delta\alpha \Delta T V_f}{b d (1 - V_f)}} \quad 7.7$$

in which G_m refers to the shear modulus of the Ti6Al4V matrix, and D_{TiB} denotes the equivalent diameter of the TiB phase. The Burgers vector of the Ti6Al4V matrix is represented by b_m , while γ describes the interspacing between the TiB particles. The true strain at the yield point of Ti6Al4V is expressed as ε_m . Additionally, k , a constant valued at 1.25, is introduced to account for geometric factors. The difference in thermal expansion coefficients between titanium and TiB is captured by $\Delta\alpha$, and ΔT represents the temperature differential between the processing conditions and the tensile testing environment. Table 7-3 summarizes the above parameter values.

7.4.3.4 Extra structure strengthening

The combined strengthening mechanisms contributed approximately 113MPa to the yield strength (σ_{ys}), still falling short by 103MPa compared to the observed increase of 216MPa. This suggests that the TiB network structure plays an additional role in enhancing strength. Similar conclusions were reached by Wang (R. Wang et al., 2023) and Li (N. Li et al., 2022), who also reported that such network structures significantly improve material strength. For alloys with a heterogeneous structure, comprising both hard and soft phases, it has been theorized that geometrically necessary dislocations (GNDs) originating from a Frank-Read source in the soft micro-regions can migrate toward grain boundaries during deformation (Y. Zhu & Wu, 2019). As deformation progresses, GNDs accumulate near the grain boundaries, and the resulting superposition of their stress fields creates a long-range internal stress, often referred to as back stress, within the soft phase. This back stress strengthens the soft regions, thereby enhancing the overall strength of the alloy (Ozerov et al., 2017). In Ti6Al4V, GNDs located near the grain boundaries are not highly active during the early stages of deformation, leading to only minimal GND accumulation at later stages, as illustrated in Figure 7-14(a). Unfortunately, due to the low density of GNDs, the strain gradient and corresponding back stress are insufficient to significantly strengthen Ti6Al4V. However, with the in-situ synthesis of TiB at grain boundaries, a more prominent GND accumulation and strain gradient occur at both the initial and later stages of deformation, particularly at the network boundaries formed by the hard phase, as shown in Figure 7-14(b). This leads to the formation of back stress within the grains, providing additional strengthening to the boron-modified alloys.

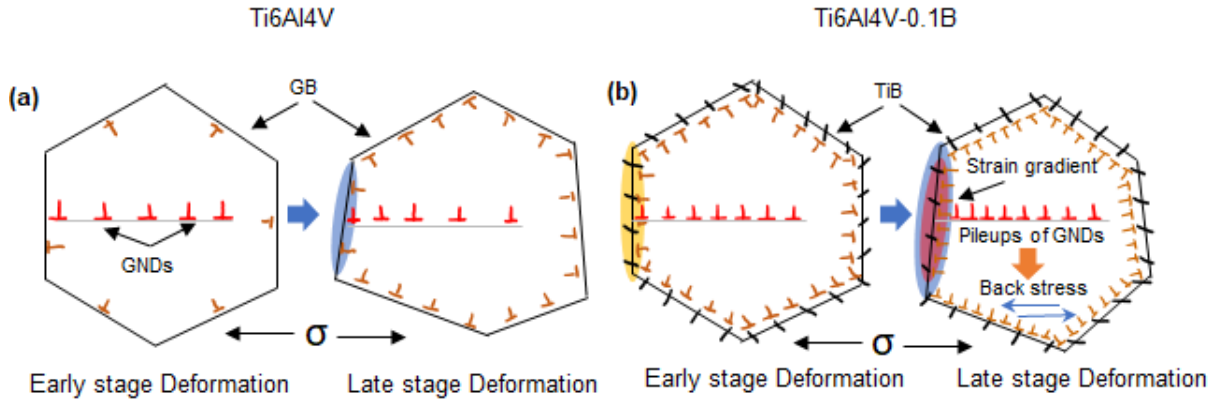


Figure 7-14 Schematic illustration showing the movement of geometrically necessary dislocations (GNDs) towards the grain boundaries during both the early and late stages of deformation in (a) Ti6Al4V and (b) boron-modified alloys. The accumulation of GNDs results in the development of back stress.

The additional strengthening contribution from the network structure ($\Delta\sigma_{stru}$) can be determined using the following equation:

$$\Delta\sigma_{stru} = \sigma_y - \Delta\sigma_{HP} - \Delta\sigma_{TiB} - \Delta\sigma_{dis} \quad 7.8$$

The contributions to the overall strength were attributed to various strengthening mechanisms, with $\Delta\sigma_{\text{stru}}$, $\Delta\sigma_{\text{HP}}$, $\Delta\sigma_{\text{dis}}$, and $\Delta\sigma_{\text{TiB}}$ offering increases of 96MPa, 68MPa, 44MPa, and 8MPa, respectively. These results underscore that the primary factors influencing the improvement in yield strength were the network structure and grain refinement. In contrast, the load-bearing capacity of TiB particles and dislocation strengthening had minimal impact on the overall strength enhancement.

7.5 Conclusion

Ti6Al4V and 0.1 wt%B-modified Ti6Al4V alloy samples were successfully fabricated using PBF-LB/M and subjected to a solution and aging heat treatment. The tensile properties of both as-built and heat-treated samples were evaluated at two orientations, $\theta=90^\circ$ and 0° , corresponding to the angle between the tensile axis and the substrate plane. The major findings from this study are as follows:

- A newly implemented algorithm was applied to calculate the Schmid factor and predict the most likely active slip system for each grain. The results demonstrated that for both as-built and heat-treated samples, the Schmid factor decreased as θ decreased, indicating that the 0° orientation samples exhibited higher strength.
- Boron modification, particularly in its crystalline form, had a pronounced effect on microstructure and mechanical properties. Crystalline boron was highly effective in promoting grain refinement and inducing a transition from columnar to equiaxed grains, particularly in the transverse sections. This led to a more uniform distribution of mechanical properties and improved strength.
- The primary contributors to enhanced yield strength in boron-modified alloys were grain refinement and structural strengthening, with negligible contributions from TiB particle load-bearing and dislocation strengthening mechanisms.

Overall, the study demonstrates the potential of crystalline boron-modified Ti6Al4V alloys to achieve significant improvements in strength and isotropy through microstructural control. These alloys show promise for applications where both mechanical performance and uniformity are critical.

CHAPTER 8

CONCLUSION and FUTURE WORK

8.1 General Conclusions

This thesis explored the potential of boron-modified Ti6Al4V alloys fabricated through PBF-LB/M to achieve in-situ grain refinement and enhanced mechanical properties. The research successfully demonstrated the influence of both amorphous and crystalline boron on microstructural evolution, phase transformation, and mechanical performance. The key findings and contributions of this work are summarized below:

- The addition of boron, particularly in its crystalline form, was shown to be a highly effective agent for grain refinement in Ti6Al4V alloys. This research demonstrated that even trace amounts of boron (0.1 wt.%) lead to a significant reduction in prior- β grain size and α -colony size, fostering a transition from the typically coarse, columnar grain structures seen in additively manufactured titanium alloys to a refined, equiaxed morphology. This refinement is critical for addressing anisotropic properties in PBF-LB/M produced alloys, ultimately leading to improved mechanical performance.
- A key finding of this thesis is the superior performance of crystalline boron over amorphous boron in promoting grain refinement, densification, and mechanical property enhancement. Crystalline boron induces a more uniform grain structure, enhances phase stability, and provides a more substantial reduction in texture intensity. The boron–titanium interaction, facilitated by the edge-to-edge matching between TiB particles and the β -phase, is a critical mechanism enabling this improvement. The research shows that crystalline boron-modified Ti6Al4V consistently outperforms its amorphous counterpart, particularly under longer laser exposure times and higher energy densities.
- This work developed a novel algorithm to calculate Schmid factors, enabling a deeper understanding of how grain orientation and active slip systems influence the mechanical behaviour of the material. The study revealed that boron-modified alloys, especially at 0° orientation, exhibited higher yield strength due to refined grain structures. Schmid factor analysis indicated that mechanical anisotropy in these alloys could be effectively mitigated by boron addition, with crystalline boron-modified samples showing the most

isotropic behaviour. This is of particular importance for applications where consistent mechanical properties in different directions are required.

- The research underscored the importance of optimizing PBF-LB/M process parameters to achieve the desired microstructure and mechanical properties. It was found that both laser power and exposure time play pivotal roles in controlling the grain refinement and phase distribution. Crystalline boron-modified alloys displayed superior relative density, higher hardness, and more consistent mechanical properties, particularly under higher power and longer exposure times. This highlights the need for precise control of processing conditions to leverage the full potential of boron as a grain refiner in PBF-LB/M processes.
- The analysis of strengthening mechanisms in boron-modified Ti6Al4V alloys identified grain refinement and structural strengthening as the dominant factors contributing to the enhanced yield strength. In contrast, the load-bearing effects of TiB particles and dislocation strengthening played a minimal role. This distinction is crucial for understanding how microstructural control can be harnessed to optimize the strength of PBF-LB/M produced alloys, moving beyond traditional approaches focused on dislocation and particle strengthening.

8.2 Future Works

While this research has successfully demonstrated the potential of boron-modified Ti6Al4V alloys fabricated through PBF-LB/M, several areas remain for further exploration and optimization to fully realize the material's capabilities for high-performance applications. The following future work is proposed to build upon the findings of this thesis:

- The presence of porosities in the tensile bars, as observed in this study, indicates a need for further optimization of PBF-LB/M parameters. Future work should focus on refining laser processing conditions, such as energy density, scanning strategies, and powder layer thickness, to minimize porosity and improve the overall density of the material. Advanced techniques like in-situ monitoring and adaptive scanning could be employed to detect and eliminate porosity during the build process.
- Although the addition of boron improved the yield strength of Ti6Al4V alloys, elongation and ductility could be further optimized, particularly in tensile bars where brittleness was noted. Future studies should investigate post-processing treatments, such as hot isostatic pressing (HIP) or tailored heat treatments, aimed at reducing porosity and enhancing ductility without compromising strength. Additionally, exploring the balance between boron concentration and the resulting microstructural changes may yield insights into improving elongation.
- Given the enhanced mechanical properties observed in boron-modified Ti6Al4V alloys, it is critical to assess the long-term performance of these materials under cyclic loading. Fatigue testing will provide valuable data on the durability and reliability of boron-modified alloys, especially in applications where they are subjected to repeated stress

cycles, such as aerospace and biomedical implants. The influence of porosity and grain structure on fatigue life should be a focal point of future investigations.

- While this thesis has established the importance of boron in refining grain structures, further microstructural characterization using advanced techniques, such as transmission electron microscopy (TEM) and 3D electron backscatter diffraction (EBSD), could provide deeper insights into the interactions between boron, TiB particles, and grain boundaries. Understanding these mechanisms at the atomic scale could guide the development of more refined alloy systems with optimized grain morphology.
- Future work could explore the synergistic effects of combining boron with other alloying elements, such as rare earth metals or silicon, to enhance both grain refinement and mechanical properties. Multi-solute additions could potentially further reduce porosity, improve ductility, and optimize the microstructure for specific applications.
- Future studies should assess the long-term behaviour of boron-modified Ti6Al4V alloys under operational conditions such as high temperatures, corrosion environments, and dynamic loading. Evaluating the stability of microstructure, mechanical properties, and phase transformations over time will be crucial to understanding the real-world applicability of these alloys in demanding industries like aerospace and biomedical engineering.

By addressing these areas, future research can further enhance the performance and applicability of boron-modified Ti6Al4V alloys, optimizing their properties for use in advanced additive manufacturing and high-performance engineering applications.

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