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Master thesis

**Electron Powder Bed Fusion of Ti-6Al-4V-Cu alloy:  
processability and microstructure analysis**

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July 2026



## Abstract

Additive Manufacturing (AM), and in particular Electron Beam Powder Bed Fusion (EB-PBF), has emerged as a transformative route for producing high-performance metallic components with complex geometries and tailored microstructures. Among structural alloys, Ti-6Al-4V remains the benchmark system due to its exceptional strength-to-weight ratio, corrosion resistance, and biocompatibility. However, its widespread application in AM is still limited by the formation of columnar prior- $\beta$  grains, strong crystallographic texture, and resulting mechanical anisotropy, which originate from steep thermal gradients and directional solidification. This study investigates the processability, microstructural evolution, and structure-property relationships of a Ti-6Al-4V-Cu alloy fabricated via EB-PBF with in-situ alloying. The primary objective is to elucidate the coupled interaction between EB-PBF thermal conditions and Cu-induced solute effects, and to determine how this interaction governs solidification behavior, phase evolution, and mechanical performance. A comprehensive experimental methodology combining Optical Microscopy (OM), Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDS), X-ray Diffraction (XRD), nanohardness testing, and in vitro bioactivity assessment was employed to establish a multi-scale understanding of the material response. The results demonstrate that Cu acts as an active thermodynamic modifier of solidification rather than a passive alloying element. Owing to its limited solubility in titanium, Cu induces strong constitutional undercooling ahead of the solid-liquid interface, increasing nucleation frequency and suppressing epitaxial grain growth. When combined with the inherently reduced thermal gradients and elevated preheating conditions of EB-PBF, this effect promotes a pronounced columnar-to-equiaxed transition (CET), leading to a predominantly equiaxed prior- $\beta$  grain structure. Microstructural analysis confirms the presence of localized Cu-enriched regions and the formation of  $\text{Ti}_2\text{Cu}$  intermetallic precipitates, arising from solute rejection during rapid solidification and repeated thermal cycling. XRD results further validate phase evolution, indicating the coexistence of  $\alpha$ ,  $\beta$ , and  $\text{Ti}_2\text{Cu}$  phases, along with lattice parameter modifications associated with Cu incorporation. Mechanical characterization through nanohardness mapping reveals a significant increase in hardness for the Cu-containing alloy compared to the base Ti-6Al-4V. This enhancement is attributed to the synergistic contributions

of solid-solution strengthening, precipitation hardening via  $\text{Ti}_2\text{Cu}$  phases, and modified grain morphology, despite partial microstructural coarsening. Bioactivity evaluation in simulated body fluid (SBF) confirms that both alloys exhibit hydroxyapatite formation, indicating good bioactive response. The Cu-containing alloy shows comparable or enhanced surface reactivity, suggesting that Cu addition does not compromise biocompatibility while introducing potential antibacterial functionality. Overall, this work establishes a clear process–structure–property relationship for Ti–6Al–4V–Cu fabricated via EB-PBF. It demonstrates that controlled in-situ alloying, combined with tailored thermal conditions inherent to EB-PBF, provides an effective pathway to engineer grain morphology, phase constitution, and functional performance. The findings contribute to advancing the design of next-generation titanium alloys with improved isotropy, enhanced mechanical response, and multifunctional biomedical capability.

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# Chapter 1

## Introduction

Additive Manufacturing (AM) is an advanced manufacturing paradigm in which components are fabricated directly from digital models through layer-wise material consolidation. By eliminating the constraints of conventional tooling, AM enables the production of geometrically complex structures such as internal channels, lattice architectures, and topology-optimized designs [1]. Beyond geometric freedom, AM establishes a direct coupling between process conditions, thermal history, and microstructural evolution, enabling simultaneous control of shape and material properties [2].

Among metallic AM technologies, Powder Bed Fusion (PBF) is one of the most widely adopted due to its high dimensional accuracy and ability to produce refined microstructures. In PBF, thin powder layers are selectively melted by a high-energy beam and solidified sequentially to form a dense structure. Depending on the energy source, PBF is classified into Laser Powder Bed Fusion (L-PBF) and Electron Beam Powder Bed Fusion (EB-PBF), also known as Electron Beam Melting (EBM) [3,4]. Although both processes share the same layer-wise principle, their thermal conditions and energy–material interaction mechanisms differ significantly, leading to distinct solidification behaviors.

L-PBF operates under an inert gas atmosphere and is characterized by extremely high thermal gradients and rapid cooling rates. These conditions promote epitaxial grain growth, high residual stresses, and pronounced microstructural anisotropy. In titanium alloys, rapid solidification may also induce martensitic  $\alpha'$  formation, resulting in high strength but reduced ductility and directional mechanical behavior [2]. In contrast, EB-PBF operates under high vacuum conditions and incorporates elevated powder bed preheating, often close to the  $\beta$ -transus temperature of Ti alloys. This significantly reduces thermal gradients, stabilizes melt pool dynamics, and decreases cooling rates, thereby enabling a more thermodynamically stable solidification environment [3].

Titanium alloys, particularly Ti-6Al-4V, are among the most widely used materials in AM due to their high specific strength, corrosion resistance, and biocompatibility. However, their microstructure is highly sensitive to thermal history. Rapid thermal cycles promote epitaxial growth of prior- $\beta$  grains along the build direction, leading to columnar grain morphologies and strong crystallographic texture. This microstructural anisotropy remains one of the key limitations of AM titanium components, directly affecting mechanical reliability and structural performance [4].

From a solidification standpoint, microstructure formation is governed by the interaction between the thermal gradient ( $G$ ) and the solidification rate ( $R$ ). Their ratio ( $G/R$ ) controls the stability of the solid-liquid interface: high  $G/R$  conditions favor directional columnar growth, whereas reduced  $G/R$  promotes nucleation and equiaxed grain formation [5]. However, in AM processes, the highly localized and transient nature of heat input makes precise control of  $G$  and  $R$  extremely challenging, resulting in spatially varying thermal fields and non-uniform microstructures.

Within this framework, EB-PBF offers a distinct advantage for microstructural control. The combination of high vacuum and elevated preheating reduces thermal gradients and improves melt pool stability, thereby shifting solidification conditions toward lower  $G/R$  regimes. This increases the probability of heterogeneous nucleation and enables the possibility of columnar-to-equiaxed transition (CET), which is essential for reducing anisotropy and improving mechanical isotropy in additively manufactured titanium alloys [1,6].

An emerging strategy to further enhance microstructural control is in-situ alloying, in which elemental powders are combined during processing instead of using pre-alloyed feedstock. This approach enables greater compositional flexibility but introduces additional complexity related to powder mixing, solute redistribution, and non-equilibrium solidification behavior.

Copper (Cu) is a particularly important alloying addition in titanium systems due to its strong influence on solidification behavior. Owing to its limited solubility in Ti, Cu is rejected into the liquid during solidification, leading to solute enrichment ahead of the solid-liquid interface. This induces constitutional undercooling, which increases the nucleation driving force and promotes grain refinement. As a result, Cu addition can destabilize epitaxial columnar growth and facilitate equiaxed grain formation [6-7].

Beyond its metallurgical role, Cu also provides functional advantages, particularly antibacterial properties, making Ti-Cu alloys attractive for biomedical applications. However, Cu addition may also lead to microsegregation and intermetallic formation under non-equilibrium solidification conditions, potentially affecting microstructural uniformity and mechanical performance.

Despite extensive research on Ti-6Al-4V processing and Ti-Cu alloy systems, the coupled interaction between EB-PBF thermal conditions and in-situ Cu alloying remains insufficiently understood. In particular, the mechanisms governing solute redistribution, melt pool dynamics, and columnar-to-equiaxed transition under EB-PBF conditions have not yet been fully clarified. A predictive understanding of how process parameters and alloy chemistry interact to control microstructure is still lacking [4].

Accordingly, this study investigates the processing of Ti-6Al-4V –Cu via Electron Beam Powder Bed Fusion, with the aim of elucidating the combined effects of Cu addition and process thermal conditions on chemical homogeneity, solidification behavior, and microstructural evolution. By leveraging the intrinsic thermal characteristics of EB-PBF and solute-driven effects of Cu, this work contributes to a deeper understanding of process–structure relationships in titanium alloys [3,6].

Ultimately, this research supports the development of additively manufactured titanium alloys with tailored microstructures, improved isotropy, and enhanced functional performance for advanced engineering and biomedical applications.

## Chapter 2

### State of the art

Additive Manufacturing (AM) has emerged as a transformative manufacturing paradigm in which components are fabricated directly from digital models through layer-wise material addition. This approach removes the geometric constraints of conventional subtractive and formative processes and enables the production of complex internal architectures, lattice structures, and topology-optimized components [1].

Metal AM technologies are broadly classified into Directed Energy Deposition (DED) and Powder Bed Fusion (PBF). DED involves continuous feeding of powder or wire into a localized melt pool generated by a focused energy source, enabling high deposition rates and suitability for repair and large-scale components. However, its relatively large melt pools and lower cooling rates limit microstructural refinement and dimensional precision [2].

PBF, in contrast, is a layer-wise process in which thin powder layers are selectively fused by a scanned energy source. This enables high spatial resolution, improved surface quality, and finer microstructural control. Among PBF technologies, Laser Powder Bed Fusion (L-PBF) and Electron Beam Powder Bed Fusion (EB-PBF), also known as Electron Beam Melting (EBM), are the most established processes. Despite sharing the same layer-wise principle, they differ significantly in energy source, thermal conditions, and process environment [8].

L-PBF operates under an inert gas atmosphere and is characterized by steep thermal gradients and extremely high cooling rates, typically leading to strong epitaxial grain growth, residual stresses, and pronounced microstructural anisotropy. In titanium alloys, these conditions often promote the formation of martensitic  $\alpha'$  phases, resulting in high strength but reduced ductility and anisotropic mechanical behavior [4,8].

EB-PBF operates under high vacuum conditions and incorporates elevated powder bed preheating, often approaching temperatures near the  $\beta$ -transus of titanium alloys. This significantly reduces thermal gradients and cooling rates while stabilizing the melt pool. As a result, EB-PBF provides a more thermally homogeneous environment, reducing residual stresses and enabling improved control over solidification pathways. These conditions are particularly advantageous for processing reactive materials such as titanium alloys.

As illustrated in Figure 1, the microstructural evolution in PBF processes is governed by solidification conditions, primarily the thermal gradient ( $G$ ) and the solidification rate ( $R$ ). Their ratio ( $G/R$ ) determines the stability of the solid–liquid interface and therefore the resulting grain morphology. High  $G/R$  conditions favor directional solidification and columnar grain growth, while reduced  $G/R$  promotes nucleation and equiaxed grain formation [4,7]. Due to the highly localized and transient nature of heat input in AM, precise control of these parameters is inherently challenging, often resulting in heterogeneous microstructures and anisotropic properties.

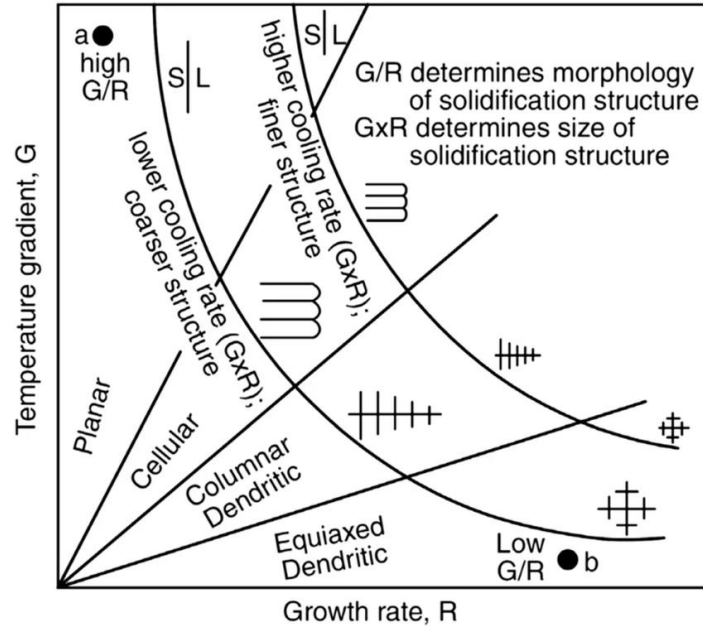


Fig. 1. Solidification map showing the effect of temperature gradient,  $G$ , and growth rate,  $R$ , on the morphology and size of solidification microstructure [8]

Titanium alloys, particularly Ti-6Al-4V, are among the most widely used materials in AM due to their high strength-to-weight ratio, corrosion resistance, and biocompatibility. However, their microstructural evolution is highly sensitive to thermal history. Rapid thermal cycles during processing promote epitaxial growth of prior- $\beta$  grains along the build direction, resulting in columnar microstructures and strong crystallographic texture. This leads to anisotropic mechanical properties that limit performance reliability in structural applications [7].

Within this framework, EB-PBF offers improved control over microstructural evolution due to its reduced thermal gradients and stable thermal environment. These conditions reduce the dominance of epitaxial grain growth and increase the likelihood of heterogeneous nucleation, creating favorable conditions for columnar-to-equiaxed transition (CET). Achieving CET is essential for reducing anisotropy and improving mechanical isotropy in additively manufactured titanium components.

An additional degree of control can be introduced through in-situ alloying, where elemental powders are combined and melted during processing rather than using pre-alloyed feedstock. This strategy expands compositional flexibility but introduces challenges related to powder mixing, solute redistribution, and non-equilibrium solidification [1,8]

Copper (Cu) is a particularly important alloying element in titanium systems due to its strong influence on solidification behavior and functional properties. Because of its limited solubility in titanium, Cu is rejected into the liquid during solidification, leading to solute enrichment ahead of the solid–liquid interface. This induces constitutional undercooling, which enhances nucleation rates and promotes grain refinement. As a result, Cu addition can destabilize columnar growth and support the formation of equiaxed grain structures [8].

In addition to its metallurgical role, Cu also imparts antibacterial properties, making Ti–Cu alloys attractive for biomedical applications. However, Cu addition may also lead to segregation and the formation of intermetallic phases under non-equilibrium solidification conditions, which can affect microstructural uniformity and mechanical performance [9].

The interaction between Cu-induced solute effects and the thermal conditions of EB-PBF is therefore critical. The reduced thermal gradients and stable melt pools in EB-PBF enhance solute redistribution and increase the effectiveness of constitutional undercooling, thereby strengthening the tendency toward equiaxed grain formation. However, the complex coupling between process parameters, melt pool dynamics, and solute behavior remains insufficiently understood for Ti-6Al-4V –Cu systems [2,10].

Despite significant progress in both AM process understanding and titanium alloy development, several fundamental aspects remain unresolved. In particular, the combined effects of EB-PBF thermal conditions and Cu addition on solute transport, solidification behavior, and microstructural evolution are not yet fully established. A predictive framework linking process parameters, alloy chemistry, and resulting microstructure is still lacking [11]. Table 1 provides an overview of the key influence of EB-PBF conditions and Cu addition on solidification and microstructure.

Table 1. Key Influence of EB-PBF Conditions and Cu Addition on Solidification and Microstructure

| <b>Factor</b>            | <b>Thermal Effect</b>                    | <b>G/R Trend</b> | <b>Microstructural Response</b> | <b>Role of Cu</b>           | <b>Outcome</b>          |
|--------------------------|------------------------------------------|------------------|---------------------------------|-----------------------------|-------------------------|
| High preheating (EB-PBF) | Reduced thermal gradients                | ↓ G/R            | Reduced epitaxial growth        | Enhances solute diffusion   | More equiaxed tendency  |
| High beam power          | Larger melt pool, slower cooling         | ↓ G/R            | Coarser grains                  | Promotes redistribution     | Lower anisotropy        |
| High scan speed          | Lower energy input, rapid cooling        | ↑ G/R            | Columnar grains                 | Limited diffusion           | Higher anisotropy       |
| Cu addition (5 wt%)      | Solute enrichment ahead of the interface | ↓ effective G/R  | Grain refinement                | Constitutional undercooling | Promotes CET            |
| Vacuum environment       | Thermal stability                        | Controlled G/R   | Uniform solidification          | Prevents oxidation          | High chemical integrity |

## 2.1 Titanium Alloys

In recent years, considerable research has focused on advancing materials tailored for biomedical, aerospace, and automotive industries. A variety of metallic materials, such as steels, cast iron, nickel-based alloys, and other metals known for their exceptional mechanical properties, have been documented for use in manufacturing within these sectors [9,10]. Nevertheless, titanium and its alloys have emerged as particularly exceptional choices due to their enhanced characteristics. Titanium alloys are composite materials primarily composed of the element titanium, which is combined with other elements such as aluminium, vanadium, and nickel to enhance their properties. These alloys are engineered to take advantage of the unique characteristics of titanium, which include its exceptional strength-to-weight ratio, corrosion resistance, and biocompatibility [12].

Titanium and its alloys represent some of the most promising materials capable of fulfilling future demands in aeroengine applications. Currently, titanium alloys are employed in the fabrication of critical components due to their superior specific strength—defined as the strength-to-density ratio—maintained up to temperatures of 600°C, surpassing that of other metallic materials (refer to Figure 2). Furthermore, titanium alloys exhibit outstanding corrosion resistance and biocompatibility, attributes that render them well-suited for use in offshore equipment, biomedical implants, and consumer products [11].

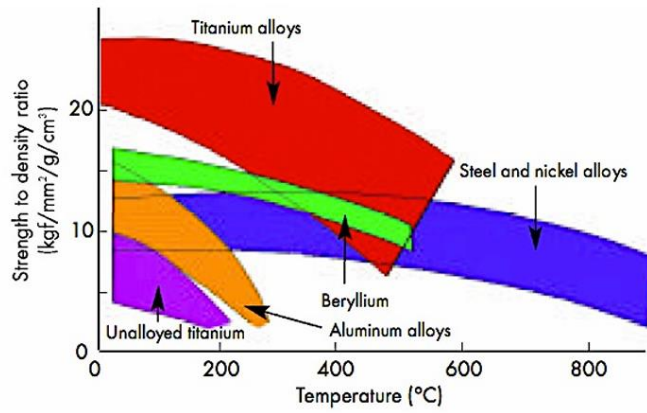


Fig. 2. Strength-to-density ratio for different metallic materials as a function of temperature. [11]

Titanium alloys are excellent options for AM, and significant efforts have been made to enhance the applications of this technology. Titanium alloys can be further categorized into different classes or groups based on their composition and properties. Some of the common classes of titanium alloys include:  $\alpha$ -titanium ( $\alpha$ -Ti) and pure titanium (cp-Ti), which exist in the  $\alpha$  phase at temperatures below 882.5°C, characterized by a hexagonal crystal lattice structure. When the temperature exceeds 883°C, the titanium alloy transitions to the  $\beta$  phase. They are often used in applications where corrosion resistance is critical, such as chemical processing equipment. The second class is related to ( $\beta$ -Ti). The  $\beta$  type contains a significant amount of  $\beta$  stabilizers in Cp-Ti and titanium alloys, which prevents the formation of intermetallic compounds like Mo, Ta, Zr, etc. Additionally,  $\beta$ -type titanium alloys can undergo heat treatment, which enhances their endurance strength. They are used in applications that require elevated temperature performance, like aircraft engine components [12,13].

Another class ( $\alpha + \beta$  Ti), which is a dual-phase  $\alpha + \beta$  alloy, the ( $\alpha + \beta$ ) phase in cp-Ti forms when the temperature exceeds 882.5°C. Additionally, the ( $\alpha + \beta$ ) phase in cp-Ti exhibits moderate strength at elevated temperatures, which is used extensively in the aerospace industry due to its high specific strength and high specific stiffness. The phase diagram of titanium and the CCT diagram for Ti-6Al-4V alloy are shown in Figure 3 [11].

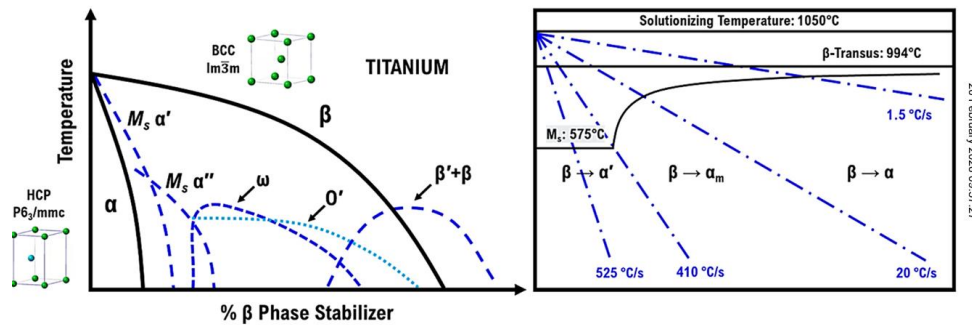


Fig. 3. Phase diagram of the titanium alloys and CCT diagram for Ti-6Al-4V alloy to show the effect of cooling rate on phase transformations. [9]

The Fig.4 systematically categorizes the paradigm shift in industrial manufacturing brought forward by AM of titanium alloys. By contextualizing twelve distinctive components across four high-performance sectors, automotive, space, aerospace, and biomedical, the figure illustrates how AM circumvents the geometric constraints inherent to traditional subtractive and formative metallurgy. The matrix demonstrates that titanium AM has transitioned from a rapid prototyping tool to a viable production method for critical, load-bearing, and fluid-dynamically optimized components operating under extreme mechanical and thermal environments.

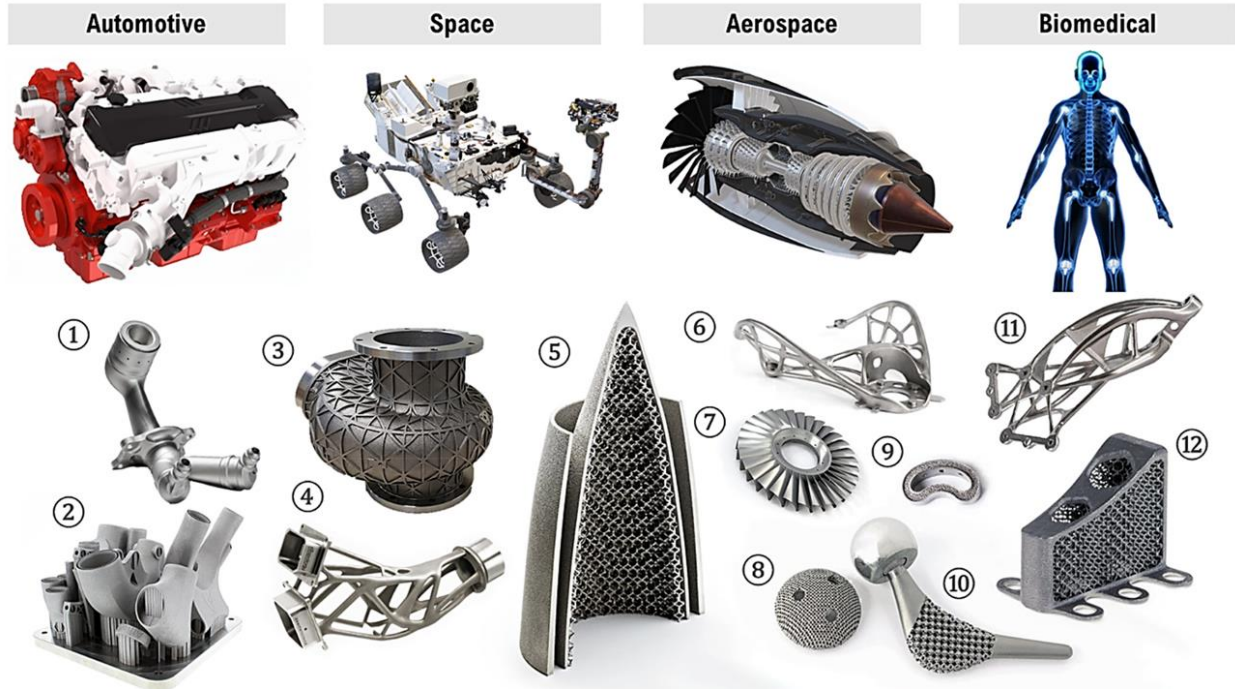


Fig. 4. Emerging applications of AM Ti alloys in various engineering disciplines, such as automotive, space exploration and rocket propulsion, aerospace and turbines, as well as biomedical load-bearing implants. [8]

From a structural engineering perspective, the components under the aerospace and space sectors highlight the practical deployment of digital topology optimization and advanced cellular structures. Components such as the satellite bracket and the trolley support bracket utilize organic, load-path-driven geometries that drastically minimize structural mass without compromising stiffness or mechanical integrity. Furthermore, the integration of macro-lattice architectures, as evidenced by the rocket tip, showcases the ability to fabricate multi-functional components capable of managing high heat fluxes while simultaneously reducing inertial weight [14].

This consolidation of parts, exemplified by the complex internal fluid pathways of the fuel nozzle and turbopump casing, directly mitigates risk by eliminating welded junctions and mechanical fasteners, thereby reducing potential failure points in high-pressure environments.

In the biomedical domain, Figure 4 highlights how the convergence of titanium's intrinsic biocompatibility and AM geometric freedom addresses complex clinical limitations. The acetabular cup, spinal implant, and hip joint feature functionally graded porous lattices that serve a dual mechanical and biological purpose. Mechanically, tailoring the porosity allows engineers to match the Young's modulus of the titanium implant to that of surrounding cortical bone, effectively mitigating the phenomenon of stress shielding and subsequent implant loosening [6,15]. Biologically, the open-cell interconnected porosity mimics natural trabecular bone architecture, optimizing the mass transport of nutrients and providing an ideal osteoconductive scaffolding that accelerates osseointegration and long-term biological fixation.

## 2.2 Additive Manufacturing (AM)

Additive Manufacturing (AM) represents a transformative manufacturing paradigm in which three-dimensional components are produced through the layer-by-layer consolidation of material directly from digital models. Unlike conventional subtractive or formative manufacturing routes, where geometry is generated through material removal or plastic deformation, AM enables the simultaneous design of both geometry and material architecture. This capability allows the fabrication of highly complex structures that would be difficult or impossible to manufacture using traditional methods, including lattice structures, internal channels, patient-specific biomedical implants, and topology-optimized components [1,12].

Beyond geometric freedom, one of the most significant advantages of AM is its ability to directly influence material microstructure during fabrication. In metallic AM processes, localized high-energy sources such as lasers or electron beams generate highly concentrated heat inputs, forming small melt pools that solidify rapidly under extreme thermal gradients. As a result, manufacturing and material formation occur simultaneously, allowing the final properties of a component to be engineered through process control rather than only post-processing [16].

A defining feature of AM is its intrinsic capability to establish a direct and hierarchical relationship between process parameters, thermal history, microstructural evolution, and resulting properties, commonly referred to as the process–structure–property (PSP) relationship. Within this framework, processing parameters such as beam power, scanning speed, hatch spacing, layer thickness, and preheating conditions determine the spatial and temporal distribution of heat input. These conditions govern thermal gradients, cooling rates, melt pool stability, and solidification kinetics, which ultimately control grain morphology, phase evolution, crystallographic texture, and chemical segregation [1,3].

Consequently, the mechanical, physical, and functional properties of additively manufactured materials are highly sensitive to processing conditions. Even minor variations in thermal history can lead to significant changes in microstructure and performance, emphasizing the importance of understanding the coupling between process parameters and material response [17].

As illustrated in Figure 5, AM establishes a strong hierarchical linkage between processing conditions, thermal history, microstructural evolution, and final properties. Process parameters directly influence heat distribution and cooling behavior, which in turn control solidification

mechanisms, phase formation, grain morphology, and ultimately the material's performance. This framework is particularly relevant to the present work, where alloy modification (Cu addition) is used as an additional parameter to control microstructural evolution under fixed EB-PBF conditions.

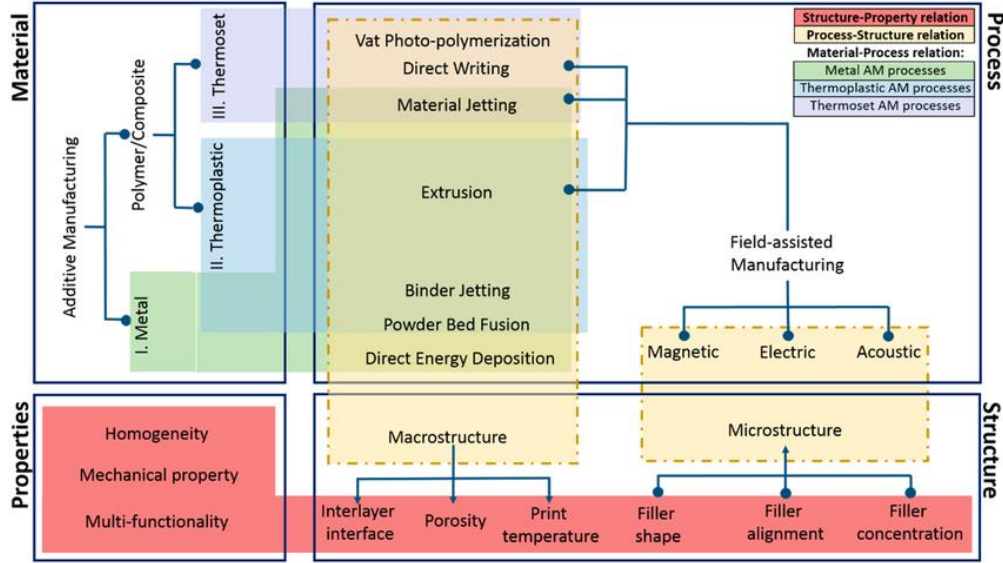


Fig. 5. Material-process-structure-property relationship classifying AM processes. [12]

Unlike conventional manufacturing methods, where microstructural control is primarily achieved through post-processing treatments such as forging, rolling, or heat treatment, AM enables in-process microstructural engineering. In this case, the thermal history is inherently embedded within the fabrication process itself, allowing continuous interaction between processing conditions and evolving microstructure [12,18].

The layer-by-layer nature of AM results in repeated thermal cycling, involving rapid melting, solidification, and reheating of previously deposited material. These cycles create highly non-equilibrium conditions characterized by steep thermal gradients, rapid cooling rates, and complex melt pool dynamics. As a result, AM processes frequently promote the formation of metastable phases, strong crystallographic texture, anisotropic grain growth, residual stresses, and local chemical heterogeneities [9,13]. While such features can be beneficial for specific applications, they also introduce challenges related to anisotropy, defect formation, and process repeatability.

Among the most critical phenomena in AM is solidification behavior, as it governs the initial grain structure that determines subsequent phase transformations and final properties. Solidification morphology is primarily controlled by the ratio of thermal gradient ( $G$ ) to solidification rate ( $R$ ). High  $G/R$  conditions typically promote columnar grain growth, whereas reduced  $G/R$  ratios favor the formation of equiaxed grains. Since grain morphology strongly influences mechanical anisotropy, fracture behavior, and overall performance, controlling solidification is a central focus in metal AM research [19].

Recent studies have demonstrated that solidification behavior can be actively manipulated not only through process optimization but also through alloy design strategies. In particular, minor alloying

additions can significantly alter constitutional undercooling, nucleation behavior, solute redistribution, and phase stability, thereby providing an effective route for controlling grain refinement and solidification pathways during AM [13,20].

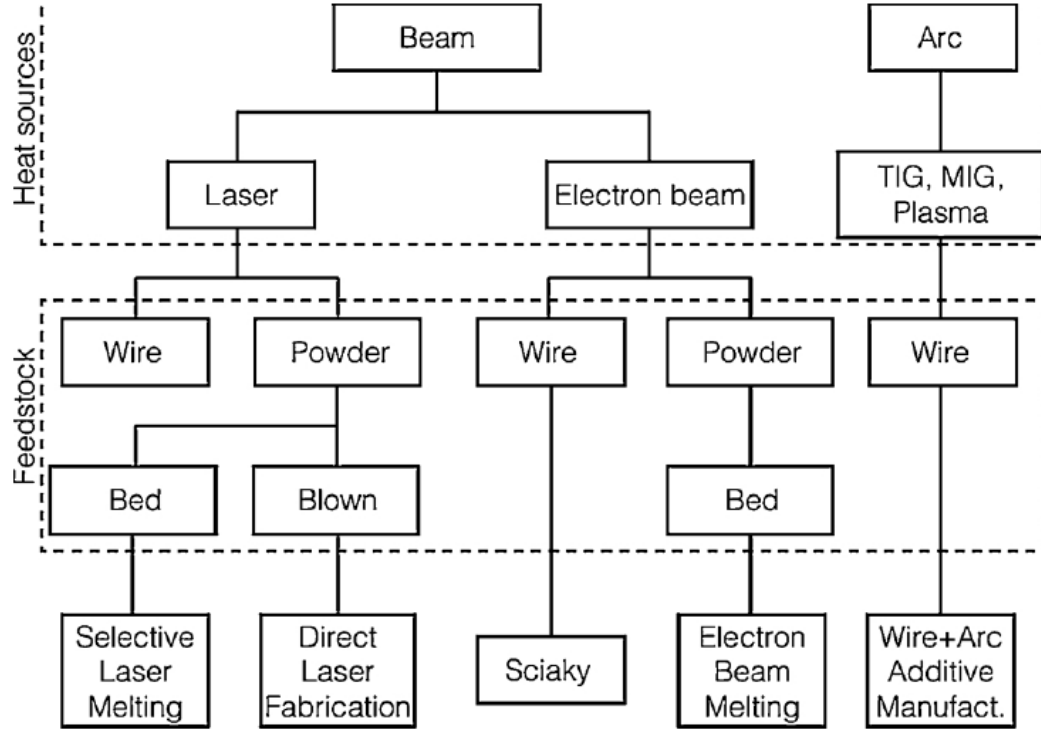


Fig. 6. Metal AM technologies available, grouped according to the heating source and the feedstock material. [14]

Figure 6 provides an overview of major metallic AM technologies, highlighting differences in energy source, feedstock type, and process environment. Among these, powder bed fusion processes offer superior control over melt pool dynamics and solidification conditions due to their localized energy input and layer-wise processing nature. In particular, EB-PBF operates under high-vacuum conditions with elevated powder-bed preheating, resulting in reduced thermal gradients, slower effective cooling rates, and enhanced thermal stability. These unique conditions significantly influence grain growth mechanisms and phase evolution, making EB-PBF especially suitable for studying alloy-driven microstructural engineering approaches [14].

Accordingly, understanding and controlling the PSP relationship is essential for ensuring reproducible microstructural development and reliable material performance. This concept forms the foundation of the present study, where the combined effect of EB-PBF thermal conditions and in-situ Cu alloying is investigated as a strategy to promote constitutional undercooling, trigger columnar-to-equiaxed transition (CET), and engineer the resulting microstructure, mechanical properties, and biofunctional performance of Ti-6Al-4V alloys [21].

### 2.2.1 Metal Additive Manufacturing Processes

Metal Additive Manufacturing processes can be broadly classified based on the mechanism of energy delivery and material deposition, with the two most established categories being Directed Energy Deposition (DED) and Powder Bed Fusion (PBF).

Although both techniques rely on localized melting and solidification, they differ fundamentally in terms of process physics, thermal control, and achievable material quality. A detailed comparison is presented in Table 2.

Table 2. General comparison of PBF and DED processes. [15]

| Criteria                               | Powder Bed Fusion (PBF)             | Direct Energy Deposition (DED)                           |
|----------------------------------------|-------------------------------------|----------------------------------------------------------|
| Build speed [ $\text{cm}^3/\text{h}$ ] | up to 170                           | up to 2000                                               |
| Max. build size (X; Y; Z) [mm]         | (0.8; 0.4; 0.5)                     | (4.0; 2.0; 1.0)                                          |
| Accuracy                               | 0.05/25                             | 0.25/25                                                  |
| Min. thickness [mm]                    | 0.2                                 | 1.0                                                      |
| Surface quality [ $\mu\text{m}$ ]      | Ra 10                               | Ra 20                                                    |
| Design Freedom                         | High                                | Low                                                      |
| Applications                           | Rapid prototyping<br>High end parts | Repairing parts<br>Adding features (i.e., ribs and lugs) |

Figure 7 clearly demonstrates that in DED processes, material in the form of powder or wire is continuously delivered into a localized melt pool generated by a focused energy source, typically a laser or electron beam. The simultaneous feeding and melting of material enable relatively high deposition rates and make DED particularly suitable for repair, cladding, and the fabrication of large-scale or functionally graded components [3,22]. However, the process is inherently characterized by larger melt pools, lower cooling rates, and reduced spatial control over heat input, which can lead to coarser microstructures, lower dimensional precision, and limited control over solidification pathways.

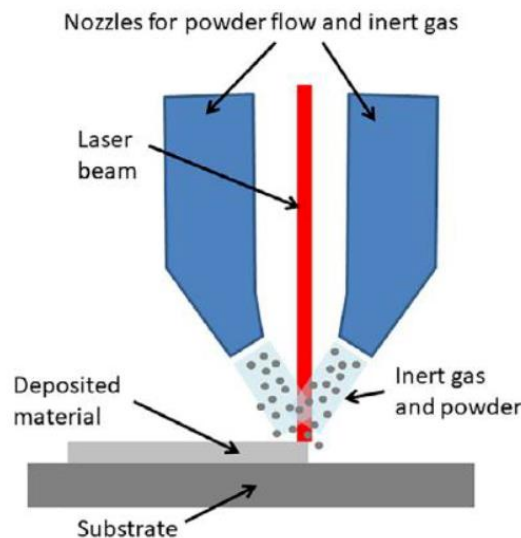


Fig. 7. Schematic representation of a blown powder system. [3]

As can be observed from Figure 8, in contrast, PBF is a layer-wise manufacturing process in which a thin powder layer is selectively fused by a scanning energy source according to the part's geometry. The process is repeated sequentially, enabling the construction of complex geometries with high precision and repeatability [1,13]. Unlike DED, PBF offers fine spatial control over energy deposition, resulting in smaller melt pools, higher cooling rates, and more localized thermal effects.

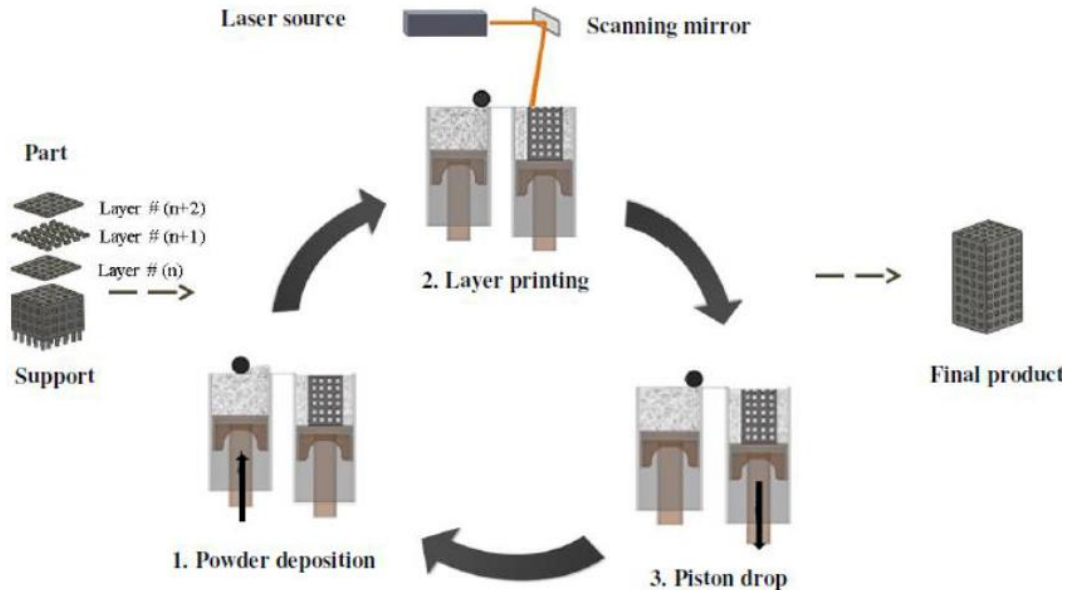


Fig. 8. Schematic representation of a powder bed process. [17]

As shown in Figure 8, PBF is therefore particularly well-suited for materials whose properties are highly sensitive to thermal history, such as titanium alloys. In this context, Ti-6Al-4V and related alloys are predominantly processed via PBF due to the following interrelated advantages:

- **Enhanced thermal control:** The layer-wise nature of PBF enables precise modulation of energy input, allowing for controlled thermal gradients and solidification kinetics.
- **Microstructural refinement:** High cooling rates promote fine microstructures, which are essential for achieving high strength-to-weight ratios.
- **Improved dimensional accuracy and surface quality:** The localized nature of melting enables near-net-shape fabrication with minimal post-processing.
- **Compatibility with reactive materials:** In the case of EB-PBF, processing under vacuum conditions minimizes oxidation and contamination, which is critical for titanium alloys [23].

Importantly, PBF—particularly EB-PBF—provides a unique capability to tailor the thermal environment at the melt pool level, enabling control over nucleation, grain growth, and solute redistribution [9]. This makes it not only a manufacturing technique but also a process-driven microstructure engineering platform, where thermal conditions can be deliberately manipulated to achieve desired microstructural states.

Within the scope of this work, this capability is of central importance, as the formation of Ti-6Al-4V-Cu alloys via in-situ alloying requires precise control over melting behavior, solute diffusion, and solidification dynamics [4,24]. The interplay between process parameters, thermal gradients, and alloy composition ultimately determines whether a columnar or equiaxed microstructure is achieved, thereby directly influencing the final mechanical and functional properties. These phenomena are schematically represented in Figure 9.

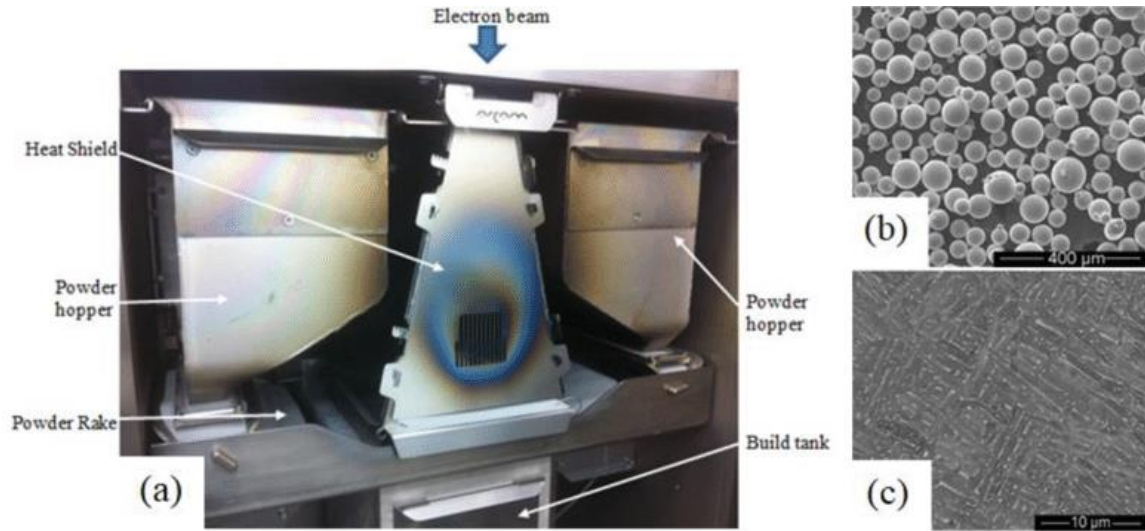


Fig. 9. Schematic drawing of an Arcam A2X electron beam melting system (a), powder image (b), and as-built Ti-6-4 ELI structure (c). [4]

### 2.3 Powder Bed Fusion (PBF) Technologies

Powder Bed Fusion (PBF) represents a class of metal Additive Manufacturing processes in which components are fabricated through the selective fusion of successive layers of powder material using a localized high-energy source [25]. As illustrated in Figure 10, the process is inherently layer-wise, where each deposited powder layer is selectively melted according to the desired geometry and subsequently solidifies before the next layer is added. This repeated sequence forms a continuous build process governed by a complex interplay between energy input, heat transfer, melt pool evolution, and solidification dynamics, which ultimately defines the resulting microstructure and defect formation [26].

Figure 10 further highlights the geometric complexity achievable in PBF, including both supported and overhanging features, which are made possible by the transient stability of the melt pool and rapid solidification behavior during layer deposition.

From a fundamental perspective, PBF can be understood as a thermally driven microstructure engineering process, where the process–structure–property (PSP) relationship is governed by highly localized and transient thermal conditions. A representative schematic of these repeated heating and cooling cycles is provided in Figure 11, which illustrates how each new layer induces partial reheating of previously solidified material [27].

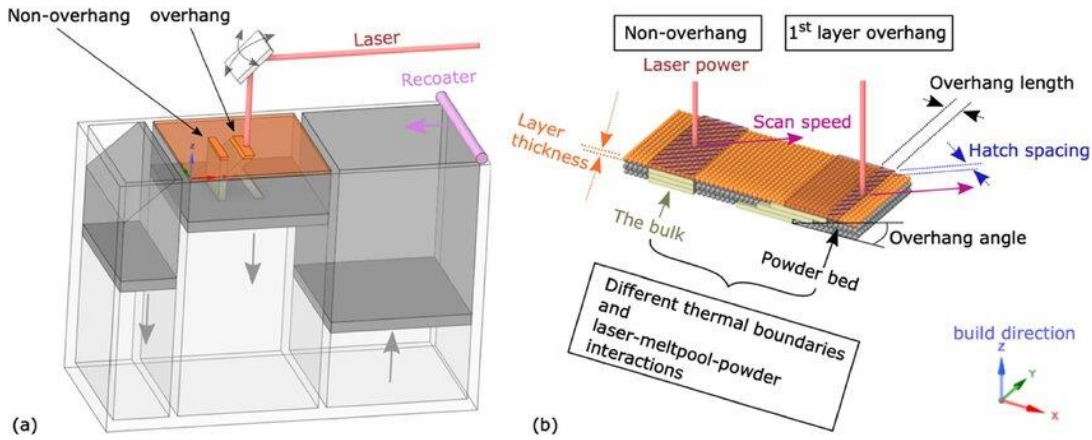


Fig. 10. (a) A schematic of the layer-by-layer process of Laser Powder Bed Fusion, showing both the non-overhang and overhang in a geometry (i.e., a letter K), and (b) the print parameters involved in producing the 1st layer overhang. [27]

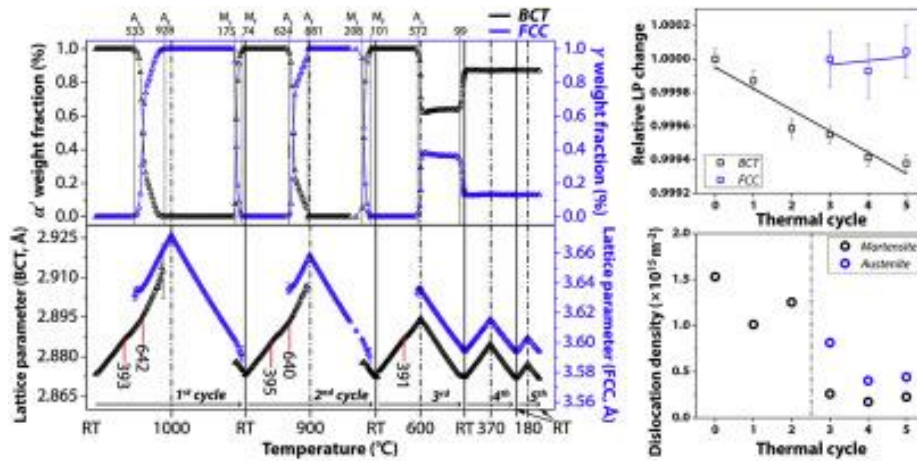


Fig. 11. Thermal cycling additive manufacturing repeated heating and cooling diagram. [28]

Figure 11 emphasizes the cyclic thermal nature of the process, where repeated heating and cooling events lead to complex thermal histories within a single build. These thermal cycles are responsible for continuous microstructural evolution, including phase transformation, grain growth, and solute redistribution in previously deposited layers [28].

Due to the localized energy input, PBF inherently produces steep thermal gradients and rapid cooling rates, leading to non-equilibrium solidification conditions. While this enables fine microstructural features, it also promotes anisotropy, residual stress accumulation, and heterogeneous grain structures. The thermal conditions shown in Figures 10 and 11, therefore, directly govern the final microstructure through their influence on melt pool stability and solidification kinetics [27-28].

### 2.3.1 Laser Powder Bed Fusion (L-PBF)

Laser Powder Bed Fusion (L-PBF) is a widely adopted metal additive manufacturing process in which a high-energy laser selectively melts successive layers of metallic powder under a controlled inert gas atmosphere. The process is characterized by highly localized energy input, which produces extremely steep thermal gradients and very rapid cooling rates, typically in the range of  $10^5$ – $10^6$  K/s. These extreme thermal conditions drive the material far from equilibrium and strongly govern solidification behavior, phase transformations, and microstructural evolution [3,14].

As a consequence of the highly confined energy input, the melt pool in L-PBF is generally small, shallow, and highly transient. Its morphology and stability strongly depend on processing parameters such as laser power, scanning speed, hatch spacing, and layer thickness. Depending on the applied energy density, the process may operate in either conduction mode or keyhole mode, each associated with distinct melt pool dynamics and defect formation mechanisms [29].

In particular, L-PBF is prone to a range of processing instabilities, including keyhole-induced porosity, balling effects, and lack-of-fusion defects, all of which are directly linked to fluctuations in melt pool geometry and thermal gradients [30]. These phenomena not only affect part density but also introduce local microstructural heterogeneities that can significantly influence mechanical performance.

Furthermore, the extremely short melt pool lifetime and limited molten volume restrict solute diffusion and redistribution during solidification. This limitation becomes especially critical in multi-component systems containing elements with limited solid solubility in titanium, such as copper. As a result, chemical partitioning and microsegregation are often frozen in place during rapid solidification, limiting the ability of L-PBF to achieve uniform compositional distribution [31]. From a microstructural standpoint, the strong directional thermal gradients inherent to L-PBF strongly promote epitaxial grain growth along the build direction, leading to the formation of elongated columnar prior- $\beta$  grains and pronounced crystallographic texture. This microstructural feature is commonly associated with anisotropic mechanical behavior and reduced structural isotropy [32].

Although L-PBF offers exceptional geometric resolution and design flexibility, its inherent thermal characteristics impose limitations in controlling grain morphology and promoting equiaxed grain formation, which are essential for achieving isotropic mechanical properties and improved functional performance [32,33]. These limitations are particularly relevant in the context of alloy design strategies based on in-situ alloying, where controlled solute redistribution and solidification pathway modification are required. Further details on melt pool geometry, stability regimes, and associated process parameters are illustrated in Figure 12.

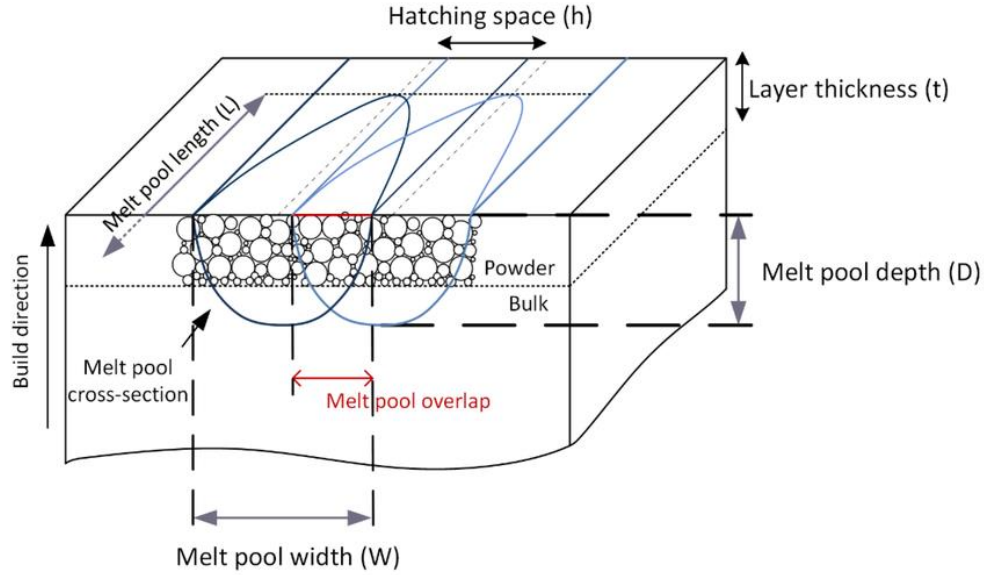


Fig. 12. Schematic representation of the melt pool and the corresponding geometric characteristics. [33]

### 2.3.2 Electron Beam Powder Bed Fusion (EB-PBF / EBM)

Electron Beam Powder Bed Fusion (EB-PBF), also known as Electron Beam Melting (EBM), is an advanced powder bed fusion technique in which a high-energy electron beam is used as the heat source under high-vacuum conditions [1]. As illustrated in Figure 13, the vacuum environment plays a critical role in enabling the processing of highly reactive metals such as titanium alloys by significantly reducing oxygen uptake, minimizing contamination, and ensuring stable high-temperature operation during fabrication.

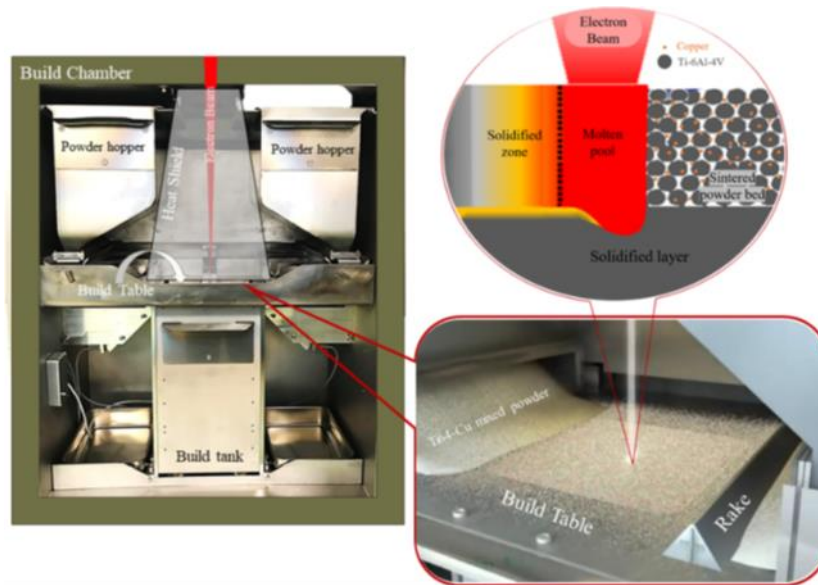


Fig. 13. Illustration of the Electron Beam Powder Bed Fusion (EB-PBF) process used in this work. [1]

A defining characteristic of EB-PBF is the elevated powder-bed preheating, which typically reaches temperatures close to the  $\beta$ -transus of Ti-6Al-4V. This preheating step fundamentally alters the thermal conditions of the process by reducing effective thermal gradients, lowering cooling rates compared to laser-based systems, and maintaining a thermally homogeneous powder bed throughout the build. As a result, the process operates under a relatively stable and heat-balanced regime, where thermal accumulation and dissipation are more evenly distributed across successive layers [1,34].

From a thermophysical and solidification standpoint, these conditions strongly influence the ratio of thermal gradient to solidification rate ( $G/R$ ), which is the key parameter governing grain morphology selection. In conventional additive manufacturing processes characterized by steep thermal gradients, solidification is dominated by epitaxial growth, leading to elongated columnar prior- $\beta$  grains aligned with the build direction. This results in strong crystallographic texture and pronounced anisotropy in mechanical properties [35]. In contrast, the reduced  $G/R$  conditions in EB-PBF weaken the dominance of directional solidification and increase the relative contribution of heterogeneous nucleation events within the melt pool. This shift creates a more favorable condition for morphological instability at the solid–liquid interface, thereby increasing the likelihood of columnar-to-equiaxed transition (CET) under suitable thermal and compositional conditions [13,36]. A graphical representation of these mechanisms is presented in Figure 14.

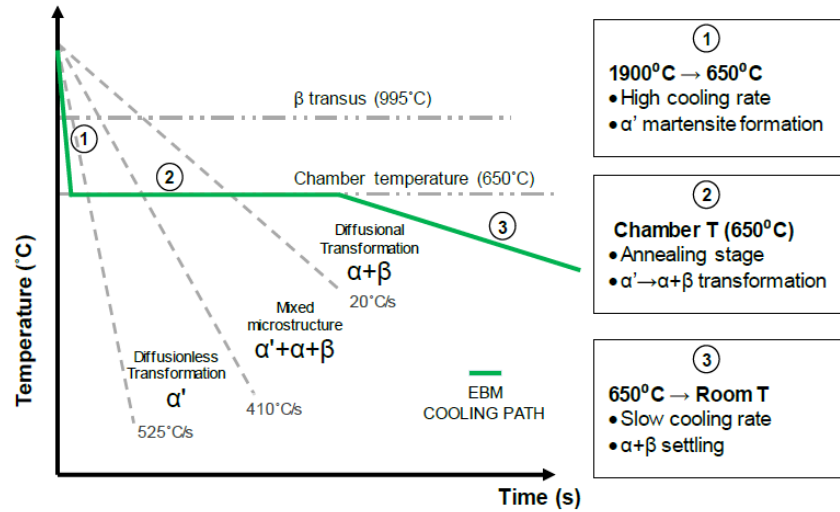


Fig. 14. General representation of the overall thermal cycle that a Ti-6Al-4V part undergoes during EBM fabrication [13].

In addition, the extended melt pool lifetime in EB-PBF, combined with reduced thermal gradients and elevated powder-bed temperatures, significantly enhances atomic mobility within the liquid phase. Compared to laser-based processes, the melt pool remains in a semi-stable state for a longer duration, allowing more time for solute diffusion, thermal homogenization, and localized chemical rearrangement before complete solidification [37]. This promotes more pronounced solute redistribution and affects the degree of microsegregation during solidification, particularly at dendritic or cellular solidification fronts.

Such effects are especially important in multi-component alloy systems, where even small compositional fluctuations can strongly influence phase stability, local undercooling conditions, and the evolution of the solid–liquid interface. In these systems, solute partitioning between solid and liquid phases can lead to the development of constitutional undercooling ahead of the advancing solidification front, which directly affects nucleation behavior and grain selection mechanisms.

As a result, the final microstructure becomes highly sensitive not only to process parameters but also to local chemical variations within the melt pool [19]. In the specific case of Ti–6Al–4V–Cu systems, these thermodynamic and kinetic conditions play a critical role in governing Cu redistribution during solidification [13,38]. Copper, having limited solubility in titanium, tends to be rejected into the remaining liquid during solidification, leading to localized Cu enrichment in interdendritic or melt pool boundary regions. Under the thermal conditions provided by EB-PBF, this redistribution is further amplified by the extended solidification time, promoting the formation of Cu-rich zones that act as preferential sites for the nucleation of  $\text{Ti}_2\text{Cu}$  intermetallic phases. These phases, in turn, contribute to precipitation strengthening and local modification of deformation behavior, while also influencing grain boundary stability and microstructural heterogeneity [39].

Overall, these characteristics make EB-PBF a particularly suitable process for microstructural engineering of titanium alloys, as it provides a precisely controllable thermal environment that directly governs grain morphology, phase evolution, and solidification pathways. Importantly, unlike conventional manufacturing routes where microstructure is primarily adjusted through post-processing, EB-PBF enables in-process microstructural control, where thermal history itself becomes a design parameter that actively shapes the final material architecture [5,40].

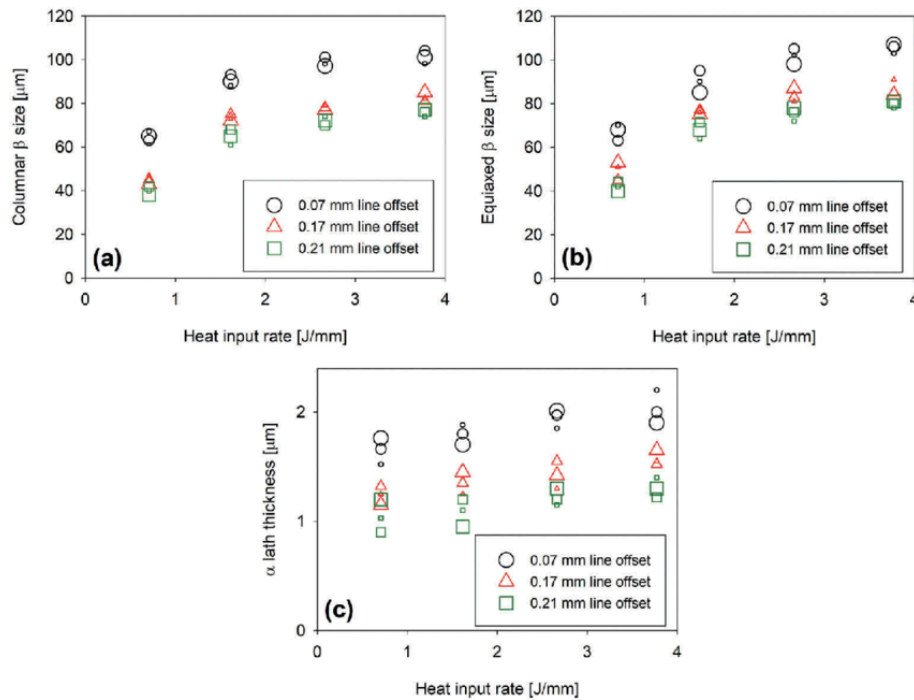


Fig. 15. (a) Columnar  $\beta$  size, (b) equiaxed  $\beta$  size, and (c)  $\alpha$  lath thickness of the samples as a function of the heat input rate. [5]

As shown in Figure 15, variations in heat input rate have a direct and measurable influence on key microstructural features such as prior- $\beta$  grain size, equiaxed grain fraction, and  $\alpha$ -lath thickness, demonstrating the strong sensitivity of titanium alloys to thermal input conditions during processing [5]. This further reinforces the concept that EB-PBF functions not merely as a fabrication technique, but as a process–structure engineering platform, where solidification pathways and resulting microstructures can be systematically tailored through the combined control of process parameters and alloy design strategies. A detailed comparison of Thermal and Process Characteristics in L-PBF and EB-PBF is given in Table 3.

Table 3. Comparison of Thermal and Process Characteristics in L-PBF and EB-PBF

| Aspect                         | L-PBF                          | EB-PBF                                  | Key Implication                                        |
|--------------------------------|--------------------------------|-----------------------------------------|--------------------------------------------------------|
| <b>Energy source</b>           | Laser (photon-based)           | Electron beam (electron-based)          | Different energy–material interaction                  |
| <b>Processing environment</b>  | Inert gas (Ar/N <sub>2</sub> ) | High vacuum                             | Eliminates oxidation in Ti alloys                      |
| <b>Powder bed temperature</b>  | Low (near ambient)             | High preheating ( $\approx$ 600–1000°C) | Strong reduction of thermal gradients                  |
| <b>Thermal gradient (G)</b>    | Very high                      | Moderately low                          | Controls directional vs non-directional solidification |
| <b>Solidification rate (R)</b> | Very high                      | Moderate                                | Influences nucleation and grain growth                 |
| <b>G/R ratio</b>               | High                           | Tunable / reduced                       | Governs columnar $\rightarrow$ equiaxed transition     |
| <b>Melt pool size</b>          | Small, shallow                 | Larger, more stable                     | Affects heat distribution and stability                |
| <b>Thermal stability</b>       | Low                            | High                                    | Reduces process fluctuations in EB-PBF                 |
| <b>Cooling behavior</b>        | Rapid and localized            | Controlled and prolonged                | Enables equilibrium-like transformations               |
| <b>Heat accumulation</b>       | Limited                        | Significant                             | Leads to layer-wise thermal homogenization             |

### 2.3.3 Process Parameters in PBF

In PBF, microstructural evolution is governed by the interaction between process parameters and the resulting transient thermal field. Unlike conventional processing, PBF involves highly localized energy input and rapid thermal cycling, producing steep thermal gradients, repeated melting–solidification events, and heat accumulation effects throughout the build [41].

The primary parameters—beam power, scan speed, hatch spacing, layer thickness, and preheating temperature—collectively define the effective energy input and thus the thermal boundary

conditions controlling melt pool formation and solidification behavior. These parameters are intrinsically coupled and cannot be considered independently [17,20].

A key descriptor of this interaction is the energy density, which reflects the balance between energy input and scan kinematics. Figure 16 reveals that increased energy input (high power or low scan speed) promotes larger and more stable melt pools with reduced cooling rates, whereas reduced energy input leads to rapid solidification and higher thermal gradients [6]. Hatch spacing and layer thickness further influence energy distribution through track overlap, where insufficient overlap results in lack-of-fusion defects and excessive overlap promotes overheating and keyhole instability.

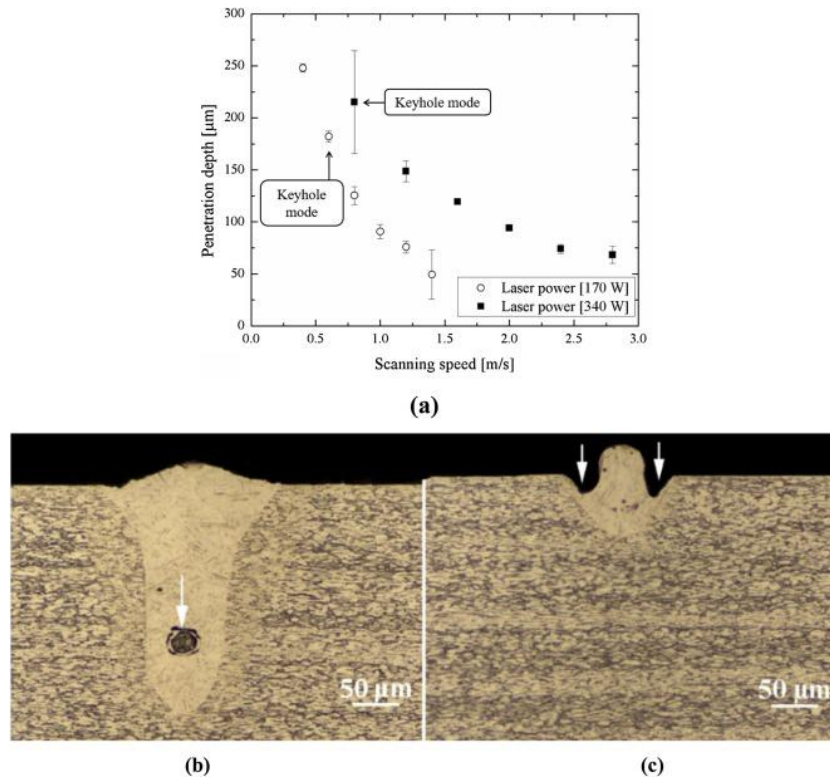


Fig. 16. (a) Penetration depth of Ti6Al4V(ELI)-3 at.% Cu single tracks versus scanning speeds; cross-sections of single tracks manufactured with laser power and scanning speeds of (b) 170 W, 0.4 m/s, and (c) 340 W, 2.8 m/s. (b) Trapped porosity within the melted pool (keyhole mode), and (c) undercuts/grooves formed with the shape of a notch at both sides of the track when humping/balling effects started (indicated by the arrows). [6]

From a solidification perspective, microstructure is primarily governed by the thermal gradient ( $G$ ) and solidification rate ( $R$ ), which are directly dictated by the process conditions. Their ratio ( $G/R$ ) determines grain morphology: high  $G/R$  favors epitaxial columnar growth, while reduced  $G/R$  enhances nucleation and promotes equiaxed grain formation. Thus, process parameters indirectly control microstructure through their influence on thermal conditions [42].

As shown in Figure 17, the melt pool acts as the central thermal system where these interactions occur. Its stability is critical for ensuring consistent solidification; stable melt pools promote uniform microstructures, whereas instability leads to defects such as porosity, balling, and lack of fusion.

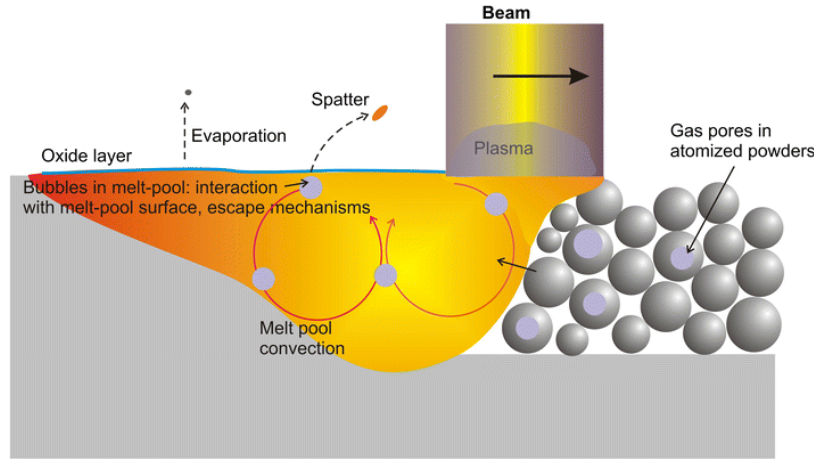


Fig. 17. Schematic illustration of melt pool phenomena during powder bed melting. [7]

In EB-PBF, elevated preheating combined with vacuum conditions reduces thermal gradients and stabilizes heat flow within the powder bed. This leads to a lower  $G/R$  ratio, which governs solidification morphology during processing. As a result, solute redistribution is enhanced, and the dominance of epitaxial grain growth is reduced, increasing the tendency toward columnar-to-equiaxed transition under suitable thermal conditions. These characteristics enable effective control of microstructural evolution in titanium alloys, directly influencing grain morphology and structural homogeneity [22,43]. Table 4 clearly demonstrates the condensed Process–Thermal–Microstructure Relationships in EB-PBF of Ti-6Al-4V –Cu.

Table 4. Condensed Process–Thermal–Microstructure Relationships in EB-PBF of Ti-6Al-4V –Cu

| Parameter / Condition           | Thermal Effect                           | G/R Trend | Microstructural Response | Role of Cu (wt%)                      | Key Outcome                                      |
|---------------------------------|------------------------------------------|-----------|--------------------------|---------------------------------------|--------------------------------------------------|
| <b>High beam power</b>          | Increased melt pool size, slower cooling | ↓ G/R     | Coarser columnar grains  | Promotes solute redistribution        | Reduced anisotropy, coarser structure            |
| <b>High scan speed</b>          | Reduced heat input, rapid cooling        | ↑ G/R     | Fine columnar grains     | Limited diffusion → segregation risk  | Higher anisotropy, potential defects             |
| <b>High preheating (EB-PBF)</b> | Reduced thermal gradients                | ↓ G       | ↓ G/R                    | Enhances Cu diffusion and homogeneity | Promotes equiaxed grains, lowers residual stress |

|                                 |                                                |                |                                      |                                          |                                         |
|---------------------------------|------------------------------------------------|----------------|--------------------------------------|------------------------------------------|-----------------------------------------|
| <b>Optimized energy density</b> | Stable melt pool                               | Tunable G/R    | Transition in grain morphology       | Facilitates uniform Cu incorporation     | Balanced mechanical properties          |
| <b>Cu addition (in-situ)</b>    | Alters local solidification via solute effects | ↓ local G/R    | Promotes constitutional undercooling | Grain refinement and equiaxed nucleation | Improved isotropy, antibacterial effect |
| <b>Vacuum (EB-PBF)</b>          | Stable thermal field, no oxidation             | Controlled G/R | Reproducible microstructure          | Prevents Cu oxidation                    | High purity, process stability          |

## 2.4 Titanium Alloys in Additive Manufacturing

Titanium alloys are among the most important material systems in Additive Manufacturing due to their high specific strength, corrosion resistance, and biocompatibility, making them ideal for aerospace and biomedical applications. Among these, Ti-6Al-4V is the most widely studied alloy, serving as a benchmark system for understanding process–structure–property relationships in AM [21].

Its  $\alpha + \beta$  microstructure provides a favorable balance between strength and ductility, but is highly sensitive to thermal history. In PBF processes, the rapid and repeated thermal cycles induce non-equilibrium conditions that strongly influence phase transformations, grain morphology, and defect formation [44].

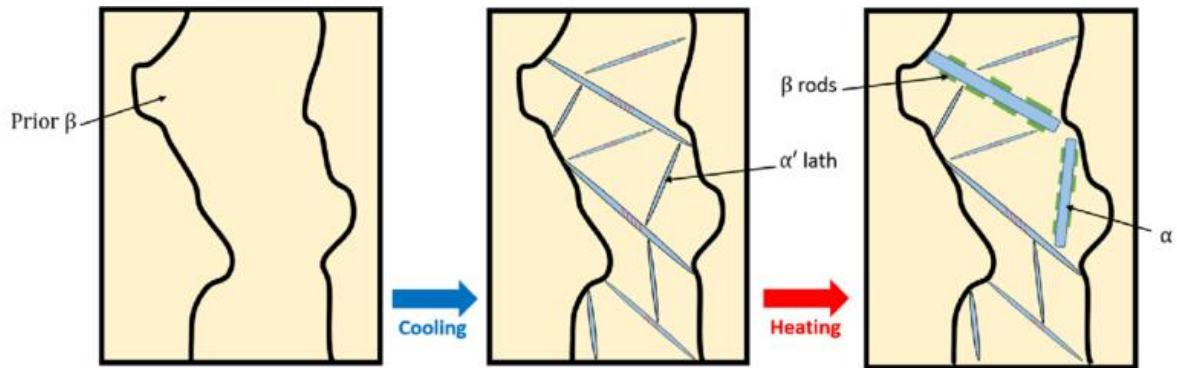


Fig. 18. Schematic of solid-state phase transformation of AM Ti-6Al-4V. [37]

As indicated in Figure 18, a major challenge in AM of Ti-6Al-4V is the formation of anisotropic microstructures, characterized by elongated columnar prior-β grains and strong crystallographic texture along the build direction. This behavior is governed by directional solidification under high thermal gradients (high G/R), which promotes epitaxial grain growth and limits nucleation [37].

Controlling this anisotropy requires precise thermal management. In this context, EB-PBF provides a more favorable processing environment due to elevated preheating and vacuum conditions, which reduce thermal gradients and stabilize the melt pool. These conditions promote

enhanced solute redistribution and increase the likelihood of columnar-to-equiaxed grain transition [24,45]

Furthermore, in-situ alloying strategies, particularly with Cu, expand the compositional design space of titanium alloys. Copper addition promotes constitutional undercooling, enhancing nucleation and grain refinement, while also introducing functional benefits such as antibacterial properties [46]. However, its limited solubility necessitates careful control of processing conditions to avoid segregation and secondary phase formation.

## 2.5 Powder Characteristics and Alloying Strategy

Powder characteristics define the initial physical and chemical state of the feedstock in PBF and therefore play a critical role in governing energy absorption, melt pool stability, and subsequent microstructural evolution. Key attributes such as particle morphology, flowability, packing density, and chemical homogeneity directly influence powder spreading behavior and the uniformity of deposited layers [23].

Particle morphology is particularly important, as spherical powders—typically produced via gas or plasma atomization—exhibit superior flowability and packing efficiency due to reduced interparticle friction. This promotes uniform layer deposition and more stable thermal conditions during processing [8]. In contrast, irregular powder morphologies tend to reduce flowability, resulting in heterogeneous powder beds and an increased susceptibility to defects such as porosity and lack of fusion. These phenomena are schematically represented in Figure 19.

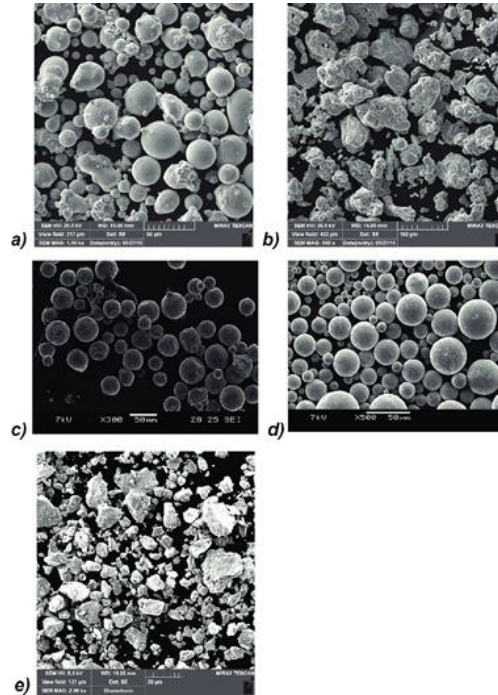


Fig. 19. SEM images of powders obtained by different technologies. (a) gas atomized In718; (b) chemical reduction Fe; (c) gas atomized Ti-6Al-4V; (d) plasma atomized Ti-6Al-4V; and (e) mechanically alloyed Fe-18Cr-8Ni-12Mn-N. [8]

Flowability and packing density collectively determine the local thermal response during processing. High packing density enhances thermal conduction and energy absorption, whereas poor packing introduces spatial variations in heat transfer and melting behavior across the build layer. Similarly, chemical homogeneity is essential to ensure consistent melting behavior and reproducible phase transformations throughout the fabricated component.

These factors become particularly critical when considering non-pre-alloyed or modified powder systems, where differences in particle size distribution and morphology can lead to segregation during powder handling and spreading. Such effects may result in local variations in powder bed composition and density, which subsequently influence melt pool stability and solidification behavior [47].

During processing, elements with lower melting points within multi-component systems tend to melt earlier and redistribute within the melt pool. Their transport is governed by diffusion and melt pool convection, both of which are strongly dependent on local thermal conditions. In such cases, solute redistribution ahead of the solidification front can alter constitutional stability, influencing nucleation behavior and solidification mode.

However, when solute elements exhibit limited solubility in the matrix phase, they may segregate during solidification and promote the formation of secondary phases or intermetallic compounds [48]. Therefore, achieving controlled microstructural evolution in PBF systems requires careful optimization of powder characteristics in conjunction with process parameters to ensure stable melting, solidification, and microstructural consistency.

## 2.6 Microstructure Evolution in Ti-6Al-4V during Additive Manufacturing

The microstructural evolution of Ti-6Al-4V in Additive Manufacturing is primarily governed by thermal gradients ( $G$ ), solidification rate ( $R$ ), and the resulting  $G/R$  ratio, which collectively control grain morphology and phase formation. During solidification, the alloy first forms the high-temperature  $\beta$  phase (BCC), which grows directionally under steep thermal gradients, producing prior- $\beta$  grains with a columnar morphology aligned along the build direction [4,26].

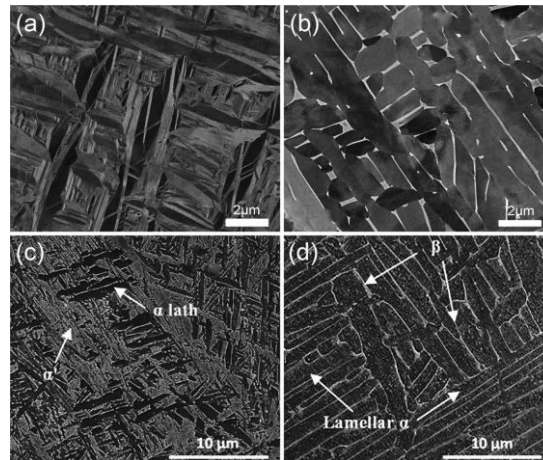


Fig. 20. Microstructures of Ti-6Al-4V alloys fabricated by (a) L-PBF, (b) EB-PBF, and (c, d) DED techniques. [43]

As shown in Figure 20, a defining feature of AM is epitaxial grain growth, where new grains inherit crystallographic orientation from the previously solidified layer. This leads to continuous grain growth across multiple layers, reinforcing strong crystallographic texture and contributing to anisotropic mechanical behavior [43].

Following solidification, the  $\beta$  phase transforms during cooling into either equilibrium  $\alpha$  (HCP) or metastable  $\alpha'$  martensite, depending on cooling rate. High cooling rates (typical of L-PBF) favor  $\alpha'$  martensite formation, resulting in high strength but reduced ductility, whereas slower cooling conditions (as in EB-PBF) promote lamellar  $\alpha + \beta$  structures with improved mechanical balance [49].

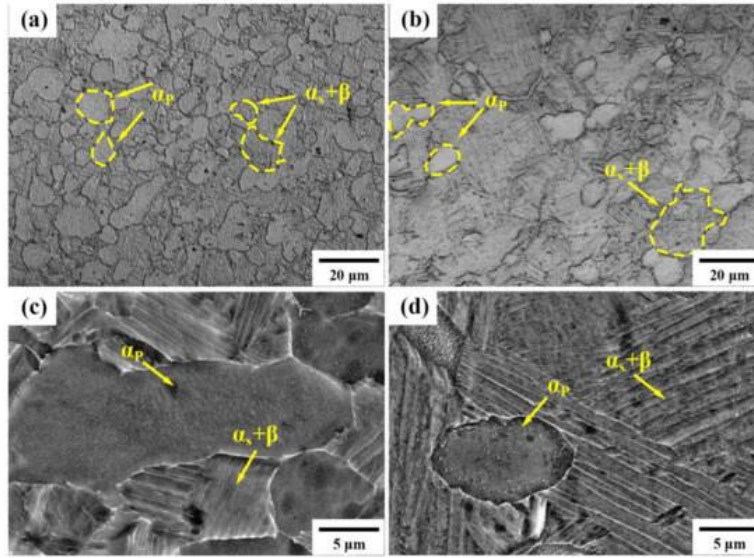


Fig. 21. Microstructural analysis of Ti-6Al-4V alloy: (a) OM and (c) SEM for the 900T sample, and (b) OM and (d) SEM for the 950T sample. [43]

EB-PBF's elevated preheating and reduced thermal gradients shift the system toward lower  $G/R$  conditions, weakening directional solidification and enhancing the likelihood of equiaxed grain formation. This thermal environment is therefore more favorable for reducing anisotropy in Ti-6Al4V.

Within this framework, Cu addition via in-situ alloying introduces an additional thermodynamic driving force [43]. Copper promotes constitutional undercooling ahead of the solidification front, increasing nucleation frequency and disrupting epitaxial grain growth. However, due to limited solubility in titanium, Cu may segregate or form intermetallic phases, requiring careful control of solidification conditions. A representative image is provided in Figure 21.

The microstructure of Ti-6Al-4V-Cu in AM is therefore the result of a coupled interaction between thermal control (EB-PBF) and solute effects (Cu), thereby enabling manipulation of grain morphology through combined process and compositional design [50].

### 2.6.1 Solidification Theory and Thermal Control

Solidification in Additive Manufacturing is governed by non-equilibrium thermal conditions, where classical equilibrium models are insufficient due to steep thermal gradients and rapid cooling rates [15]. The microstructure is primarily controlled by the thermal gradient ( $G$ ) and solidification rate ( $R$ ), whose ratio ( $G/R$ ) defines the solidification regime.

A representative image is provided in Figure 22 that shows high thermal gradients stabilize the solid–liquid interface and promote directional solidification, leading to columnar grain growth and strong texture. In contrast, reduced thermal gradients or increased solidification rates destabilize the interface, promoting nucleation and equiaxed grain formation [44].

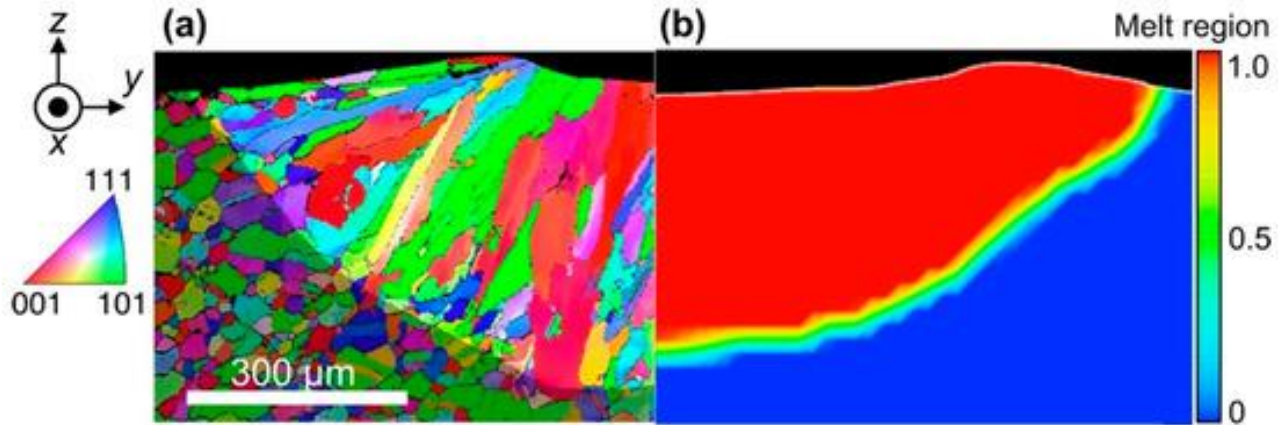


Fig. 22. Comparison of melt regions in (a) experimental SEM image and (b) CtFD simulation for the case with a beam diameter of 1200  $\mu\text{m}$ , absorption rates of 0.8, beam power ( $P$ ) of 1200 W, and beam scanning speed ( $V$ ) of 100 mm/s. [44]

The transition between these two regimes is known as the Columnar-to-Equiaxed Transition (CET), which is a key mechanism governing grain morphology in AM. CET occurs when conditions favor nucleation ahead of the solidification front, typically under low  $G/R$  conditions. In Ti-based systems, this transition is strongly influenced by process parameters and alloy chemistry. EB-PBF promotes lower thermal gradients through elevated preheating and vacuum conditions, shifting the system toward reduced  $G/R$  and more uniform solidification behavior [51].

In addition, solute elements such as Cu further modify solidification conditions by inducing constitutional undercooling, which enhances nucleation and promotes equiaxed grain formation [13]. The combined effect of thermal control of EB-PBF and solute engineering (Cu addition) provides a powerful mechanism for tuning microstructural evolution in AM.

## 2.7 In-situ Alloying in Additive Manufacturing

In-situ alloying is an advanced additive manufacturing strategy in which alloy compositions are generated directly during processing through the controlled mixing and co-melting of elemental powders [1]. Unlike conventional approaches that rely on pre-alloyed feedstock, this method enables flexible and on-demand compositional design, thereby significantly expanding the material design space available for powder bed fusion processes.

In powder bed fusion systems, the final chemical composition is not strictly predefined but evolves through the coupled interaction between powder mixing state, melt pool dynamics, and rapid solidification conditions. This inherently creates a strong interdependence between process parameters, thermal history, and resulting microstructural development [52].

A key thermodynamic mechanism governing in-situ alloying is constitutional undercooling. During solidification, solute redistribution ahead of the solid–liquid interface alters the local liquidus temperature, increasing the thermodynamic driving force for nucleation [21]. Figure 23 presents that this effect can enhance grain refinement and destabilize epitaxial columnar growth, promoting the formation of more isotropic microstructures under suitable thermal conditions.

However, in-situ alloying also introduces intrinsic challenges related to powder-scale compositional heterogeneity and solute redistribution during rapid solidification. These factors may lead to localized chemical fluctuations, non-uniform phase evolution, and spatial variations in microstructural features if not properly controlled [44].

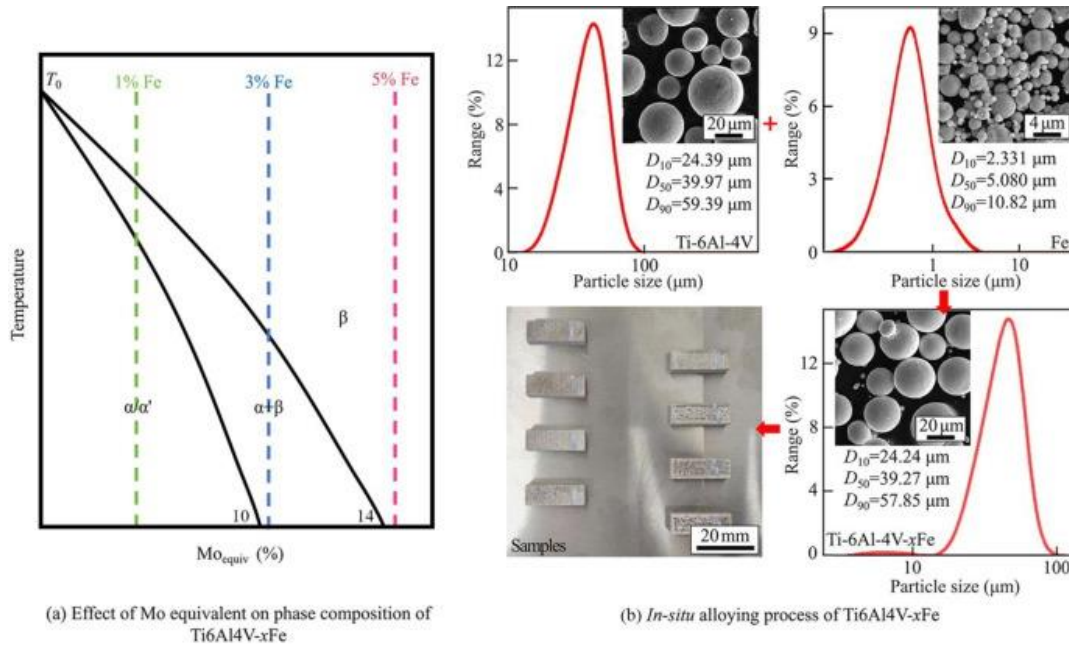


Fig. 23. Effect of Mo equivalent on phase composition of Ti6Al4V-xFe alloys and in-situ alloying process of Ti6Al4V-xFe. [44]

Importantly, the effectiveness of in-situ alloying is strongly dependent on the thermal characteristics of the manufacturing process. In EB-PBF, elevated preheating temperatures and reduced thermal gradients contribute to enhanced melt pool stability and more uniform thermal conditions, which in turn influence solute transport and mixing behavior during solidification.

In-situ alloying should be viewed as a process–structure coupled phenomenon rather than a purely compositional strategy, where material formation is governed by the interaction between alloy chemistry and the evolving thermal field during layer-by-layer fabrication [53].

## 2.8 Role of Copper (Cu) in Ti Alloys

Copper (Cu) is a key alloying element in titanium systems, particularly under additive manufacturing conditions, where it strongly influences solidification behavior, phase evolution, and microstructural refinement [8]. In Ti–Cu based systems, Cu acts primarily through solute-driven effects that modify nucleation behavior and grain growth kinetics, making it a critical parameter within the process–structure relationship of this study.

A central mechanism is constitutional undercooling, arising from the limited solubility of Cu in Ti. During solidification, Cu is rejected into the liquid ahead of the solid–liquid interface, generating a solute-enriched boundary layer that lowers the local liquidus temperature. This increases local undercooling and enhances nucleation probability, destabilizing directional growth [54].

This directly modifies the thermal gradient–solidification rate balance ( $G/R$ ). Although  $G$  and  $R$  are governed by process conditions, Cu addition effectively reduces the local  $G/R$  ratio through solute effects, promoting a transition from columnar epitaxial growth toward equiaxed grain formation. In this way, Cu acts as a compositional control parameter that complements thermal control in EB-PBF.

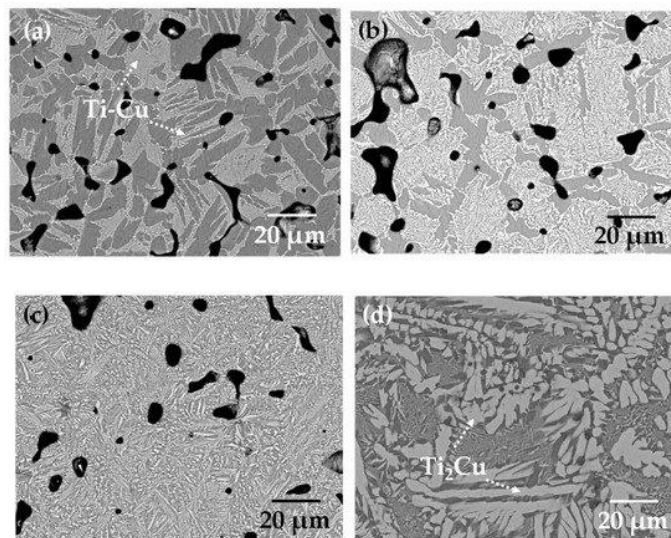


Fig. 24. SEM micrographs of the samples sintered at 1100 °C: (a) Ti64-5Cu, (b) Ti64-10Cu, (c) Ti64-15Cu, and (d) Ti64-20Cu. [45]

As can be observed from Figure 24, beyond grain morphology, Cu contributes to grain refinement by increasing nucleation density and limiting competitive columnar growth. This leads to finer microstructures and reduced crystallographic anisotropy, improving isotropy in mechanical response—an important limitation in conventional AM Ti-6Al-4V [45].

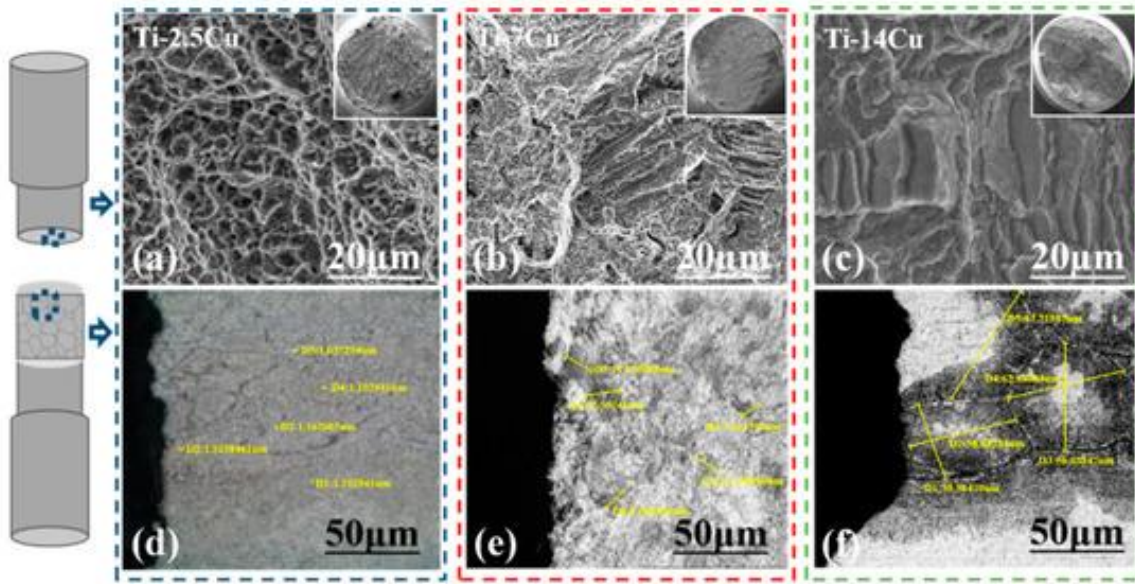


Fig. 25. Fracture morphology of Ti-Cu alloys (a) Ti-2.5Cu, (b) Ti-7Cu, and (c) Ti-14Cu, and section morphology of (d) Ti-2.5Cu alloy, (e) Ti-7Cu alloy, (f) Ti-14Cu alloy. [46]

In addition, Cu plays a direct role in facilitating the CET. Its solute-driven undercooling effect works synergistically with the reduced thermal gradients in EB-PBF, where preheating already lowers  $G$ . The combined thermal–compositional effect significantly increases the likelihood of equiaxed grain formation.

However, Cu addition also introduces microstructural complexity. Due to its limited solubility in Ti, segregation can occur during rapid solidification, potentially leading to Cu-rich regions or intermetallic phases. These features may affect mechanical consistency and must be controlled through optimized process conditions [46]. Further details can be found in Figure 25.

Overall, Cu acts as a dual-function alloying element: it enables microstructural refinement and isotropy improvement, while also introducing solute-driven segregation risks. Its effectiveness is therefore strongly dependent on the thermal conditions imposed by EB-PBF, making it a key variable in the process–structure–property framework of this thesis. Table 5 presents the Mechanisms of Cu Addition in Ti Alloys under AM.

Table 5. Mechanisms of Cu Addition in Ti Alloys under AM

| <b>Mechanism</b>                                      | <b>Observed Effect (Literature)</b>                      | <b>Microstructural Outcome</b>                      | <b>Key Limitation in EB-PBF Context</b>                      |
|-------------------------------------------------------|----------------------------------------------------------|-----------------------------------------------------|--------------------------------------------------------------|
| <b>Constitutional undercooling</b>                    | Cu enriches the liquid ahead of the interface            | Promotes heterogeneous nucleation → equiaxed grains | Critical undercooling range not quantified for EB-PBF        |
| <b>Solute partitioning</b>                            | Cu segregates due to limited solubility in Ti            | Microsegregation and local composition gradients    | Segregation behavior under EB-PBF thermal conditions unclear |
| <b>Grain refinement (AM studies on Ti–Cu systems)</b> | Increased nucleation density                             | Finer, more uniform grain structure                 | Process–composition coupling is not fully understood         |
| <b>G/R modification</b>                               | Cu effectively lowers local G/R via solute effects       | Drives columnar → equiaxed transition (CET)         | G–R–Cu interaction in EB-PBF is not established              |
| <b>Phase evolution</b>                                | Formation of Ti–Cu intermetallics reported               | Can enhance strength but may reduce ductility       | Phase stability under rapid AM solidification uncertain      |
| <b>Functional behavior</b>                            | Cu imparts antibacterial properties (biomedical studies) | Enhanced surface functionality                      | Trade-off between functionality and mechanical integrity     |

## 2.9 Research Gap

Copper is a key alloying element in titanium systems due to its strong influence on solidification behavior, phase stability, and microstructural evolution, particularly under Additive Manufacturing conditions. In Ti–Cu systems, the limited solubility of Cu in Ti leads to solute rejection during solidification, generating constitutional undercooling ahead of the solid–liquid interface. This locally reduces the liquidus temperature and increases the driving force for nucleation, thereby promoting grain refinement [55].

In the context of solidification theory, Cu modifies the effective thermal conditions by reducing the local stability of the advancing solidification front, which indirectly lowers the G/R ratio. This promotes a transition from columnar to equiaxed grain growth, especially when combined with the reduced thermal gradients characteristic of EB-PBF. Thus, Cu acts as a solute-driven control parameter that complements process-induced thermal control [3].

Beyond grain refinement, Cu addition increases nucleation density and disrupts epitaxial columnar growth, improving microstructural isotropy and reducing crystallographic texture. This is particularly important in AM Ti alloys, where strong directional solidification typically leads to anisotropic mechanical behavior [56].

However, Cu also introduces challenges due to its limited solubility in Ti, leading to possible segregation and intermetallic formation under non-equilibrium solidification conditions. These effects can locally alter mechanical response and microstructural stability, making process control

essential. Cu functions as a powerful but highly sensitive alloying element that couples solute effects with thermal conditions, making it a key factor in controlling the process–structure relationship in EB-PBF-processed Ti alloys [36]. The corresponding results are summarized in Table 6.

Table 6. Summary of Knowledge Gaps in Ti-6Al-4V –Cu EB-PBF Systems

| <b>Domain</b>                     | <b>Current Knowledge</b>     | <b>Limitation</b>            | <b>Gap</b>                      |
|-----------------------------------|------------------------------|------------------------------|---------------------------------|
| <b>EB-PBF thermal field</b>       | Lower G, high preheating     | Not quantified for Cu alloys | No G–R–Cu coupling model        |
| <b>Cu alloying behavior</b>       | Grain refinement in AM       | Mostly L-PBF / casting       | Unknown in EB-PBF               |
| <b>Melt pool dynamics</b>         | General understanding        | No Cu-specific study         | Lack of solute flow data        |
| <b>CET behavior</b>               | Theoretical framework exists | Not AM-specific              | No threshold conditions defined |
| <b>Process–structure–property</b> | Fragmented studies           | No integrated model          | Missing unified framework       |

## Chapter 3

### Materials and Methods

#### 3.1 Feedstock Design and Powder Selection

The feedstock system consists of gas-atomized Ti-6Al-4V extra-low interstitial (ELI) powder with a particle size distribution  $\leq 106 \mu\text{m}$  ( $D_{50} \approx 75 \mu\text{m}$ ) and high-purity copper powder with a median particle size of approximately  $6.6 \mu\text{m}$ . The selection of a bimodal powder system is intentional, enabling hierarchical packing behavior and promoting controlled spatial proximity between solute and matrix phases prior to melting.

Ti-6Al-4V -ELI was selected as the matrix material due to its well-established solidification behavior under electron beam powder bed fusion conditions, including predictable  $\beta$ -phase formation and subsequent diffusion-controlled transformations [57]. This provides a stable baseline system in which deviations in microstructure and mechanical response can be attributed primarily to the introduction of copper rather than intrinsic variability of the base alloy.

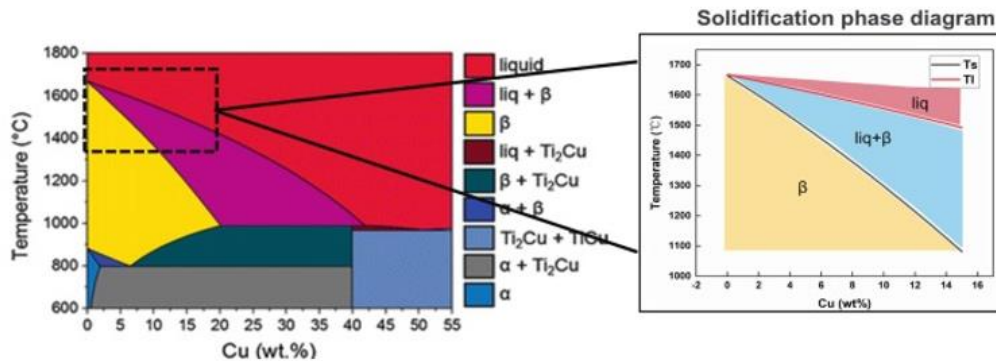


Fig. 26. Ti-Cu phase diagram showing solidus/liquidus variation with Cu content. [40]

Copper was introduced as a thermodynamically incompatible solute in titanium, characterized by negligible equilibrium solubility in  $\alpha$ -Ti and limited solubility in  $\beta$ -Ti. Its strong partitioning tendency during solidification ( $k < 1$ ) promotes solute pile-up at the solid–liquid interface, increasing constitutional undercooling and destabilizing planar solidification fronts under the high cooling rates associated with EB-PBF. As shown in Figure 26, consequently, Cu functions as a controlled perturbation element that modifies local solidification stability and enhances microsegregation phenomena [40].

The disparity in particle size between Ti and Cu powders is also critical to the designed feedstock architecture. Fine Cu particles preferentially occupy interstitial spaces within the Ti powder bed, increasing the probability of localized dissolution during melt pool formation and reducing stochastic redistribution effects during powder spreading.

### 3.2 Powder Blending and Feedstock Homogenization

Powder blending was performed using sealed jar milling for 16 hours under dry atmospheric conditions to achieve controlled mechanical homogenization without inducing excessive particle deformation or agglomeration. The primary objective of blending was not alloy formation at the powder stage, but the establishment of a metastable powder configuration that governs solute distribution during subsequent melting [2].

The blending process promotes partial adhesion of fine Cu particles onto the surface of larger Ti particles, forming a heterogeneous “satellite-assisted” powder architecture. This configuration reduces the fraction of freely mobile Cu particles, thereby suppressing segregation during recoating and improving the spatial uniformity of solute distribution within the powder bed [58].

From a mechanistic standpoint, this architecture modifies the initial boundary conditions of the thermal–chemical system by ensuring that copper is preferentially located at or near Ti particle surfaces before beam interaction. As a result, Cu dissolution occurs predominantly within the melt pool rather than through random redistribution in the powder layer, enhancing the reproducibility of solute incorporation during rapid solidification.

The blending conditions were selected to maintain a balance between sufficient interparticle interaction and preservation of powder flowability. Excessive mechanical energy input was avoided to prevent cold welding of Ti particles and the formation of Cu agglomerates, both of which would adversely affect layer deposition stability [1,58]. A representative image is provided in Figure 27.

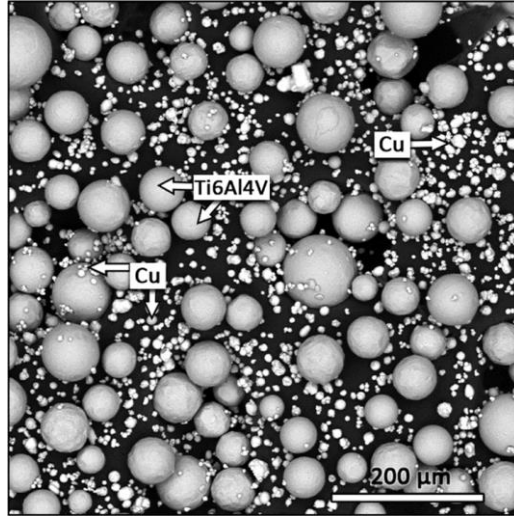


Fig. 27. Backscattered SEM image of the initial powder blend. [1]

### 3.3 Electron Beam Powder Bed Fusion (EB-PBF) Processing

As can be observed in Figure 28, all samples were fabricated using an Arcam A2X electron beam powder bed fusion system operating under high vacuum conditions. The use of a vacuum is essential in Ti–Cu systems to prevent oxygen uptake, which would otherwise alter both electron beam absorption characteristics and alloy thermodynamics.



Fig. 28. Arcam A2X Electron Beam Powder Bed Fusion system employed in this study for Ti-6Al-4V –Cu fabrication.

A standard Ti-6Al-4V build theme was employed to ensure consistent thermal input across all samples. The process was conducted at a beam acceleration voltage of 60 kV with a constant layer thickness of 50  $\mu\text{m}$ . The build chamber was maintained at a preheating temperature of approximately 750 °C to promote partial sintering of the powder bed. This preheating condition increases electrical conductivity, stabilizes beam–powder interaction, and reduces electrostatic powder scattering during layer deposition [58].

The scanning strategy consisted of a combined MultiBeam™ contour melting approach and conventional hatch scanning for bulk consolidation. The contour strategy is responsible for geometrical fidelity and surface stability, while the hatch strategy governs volumetric densification and internal microstructure formation. This separation of functions allows decoupling of surface morphology control from bulk solidification behavior. Thermally, the process is governed by repeated cyclic heating and cooling associated with layer-by-layer deposition. This results in significant thermal accumulation in the build volume, which directly influences  $\beta$ -grain growth, solute redistribution, and melt pool overlap characteristics [59].

### 3.4 Sample Extraction and Metallographic Preparation

In EB-PBF, the electron beam sinters a dense powder cake around the printed part to act as structural support and maintain thermal conductivity. After the build finishes, the entire block is transferred into this enclosed blasting cabinet, and the Powder Recovery Station (PRS) was used to clean samples (Figure 29).



Fig. 29. Powder Recovery Station (PRS), specifically the GE Additive Arcam.

After that, sectioning was performed along the Y–Z plane parallel to the build direction using wire electrical discharge machining, enabling direct observation of solidification path evolution and thermal gradient-driven microstructural development.

### 3.5 Metallography

Following sectioning along the Y–Z plane, metallographic preparation was carried out to reveal the as-built microstructure produced during Electron Beam Powder Bed Fusion. The preparation route was designed to preserve fine-scale solidification features, including melt pool boundaries, prior- $\beta$  grain structures, and chemically heterogeneous regions.

The grinding stage was performed using a Presi automatic grinding machine to ensure controlled and repeatable surface preparation conditions [60]. A sequential abrasive paper progression (P480, P600, P800, P1200, and P2400) was employed to gradually reduce surface roughness and remove deformation induced during sectioning. This step is essential for minimizing mechanically induced artifacts that could distort microstructural interpretation. Further details can be found in Figures 30 and 31.



Fig. 30. Sample mounting procedure (a) Specimens were embedded in acrylic resin using a methyl methacrylate hardener to ensure structural stability and ease of handling during subsequent metallographic preparation. (b) After curing, the mounted samples were extracted from the mould and prepared for sequential grinding and polishing.



Fig. 31. Grinding setup and abrasive sequence, (a) Metallographic grinding and polishing were performed using a Presi automatic preparation system to ensure controlled and reproducible surface finishing. (b) A progressive abrasive sequence (P480, P600, P800, P1200, and P2400) was applied to systematically reduce surface roughness and remove deformation induced during sectioning.



Fig. 32. Polishing media used for final surface preparation. Polishing was carried out using multi-stage polishing pads with 3  $\mu\text{m}$  (blue) and 1  $\mu\text{m}$  (pink) grit sizes to progressively eliminate residual surface deformation and achieve a deformation-free surface suitable for high-resolution microstructural characterization.

As shown in Figure 32, Polishing was subsequently performed using multi-stage polishing pads with 3  $\mu\text{m}$  (blue) and 1  $\mu\text{m}$  (pink) diamond grit sizes. This dual-stage approach ensures progressive removal of surface deformation while maintaining microstructural integrity.

Figure 33 shows that final polishing was performed using colloidal silica to achieve a deformation-free surface suitable for high-resolution optical and electron microscopy.

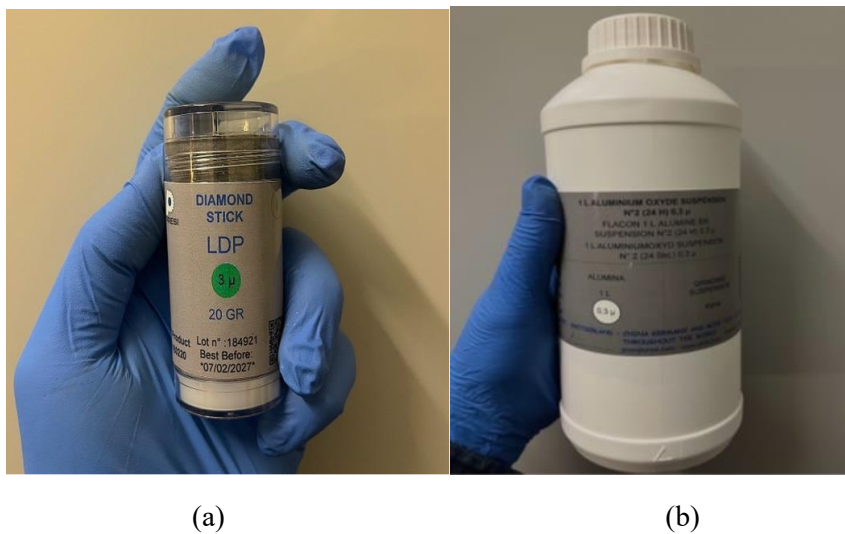


Fig. 33. Final polishing stages of metallographic preparation using (a) diamond suspension with lubricant applied on a 1  $\mu\text{m}$  polishing pad and (b) 0.3  $\mu\text{m}$  aluminium oxide slurry used with a 3  $\mu\text{m}$  pad to obtain a deformation-free surface suitable for microstructural analysis.

A combination of diamond suspension and lubricant was used during fine polishing to enhance surface finish and reduce pull-out effects in heterogeneous regions. For final refinement, a 0.3  $\mu\text{m}$  aluminum oxide solution was applied, ensuring removal of residual surface damage and enabling accurate phase and grain boundary resolution during SEM analysis.

### 3.6 Microstructural, Phase, and Chemical Characterization

A comprehensive multi-scale characterization strategy was implemented to establish direct correlations between processing conditions, thermal history, and the resulting hierarchical microstructure. The main objective was to systematically link the EB-PBF process parameters and Cu addition effects to the observed phase evolution, grain morphology, and chemical distribution across multiple length scales [61].

The combined use of optical microscopy (OM), scanning electron microscopy (SEM), X-ray diffraction (XRD), and energy dispersive spectroscopy (EDS) enabled a detailed investigation of the material structure from the macro-scale down to localized compositional variations at the microscale. Optical microscopy was used to identify global features such as melt pool geometry, layer-wise bonding characteristics, and overall defect distribution. SEM provided higher-resolution insight into microstructural constituents, including prior- $\beta$  grains,  $\alpha$ -lath morphology, intermetallic precipitates, and the spatial distribution of Cu-enriched regions formed during solidification.

XRD analysis was employed to identify and quantify the phase composition of the as-built and alloyed materials, with particular attention to the presence of  $\alpha$ -Ti, retained  $\beta$  phase, and  $\text{Ti}_2\text{Cu}$  intermetallic compounds [62]. This phase-level information is critical for understanding the thermodynamic stability of the system and the influence of Cu on phase transformation pathways under rapid solidification conditions.

In parallel, EDS was used to evaluate elemental distribution and assess the degree of chemical homogeneity achieved through in-situ alloying. Spatially resolved compositional mapping allowed the identification of solute segregation, particularly in melt pool boundary regions and interdendritic zones, where non-equilibrium solidification effects are most pronounced. This integrated characterization approach is particularly essential for Electron Beam Powder Bed Fusion systems, where rapid thermal cycling, repeated reheating, and extended melt pool lifetimes lead to complex, non-equilibrium solidification conditions. These conditions produce hierarchical microstructures characterized by a combination of macro-scale melt pool patterns, meso-scale grain structures, and micro-scale phase and compositional heterogeneities [30,41].

Each characterization technique was therefore selected to resolve a specific length scale of this complexity, enabling a comprehensive understanding of how thermal gradients, solidification dynamics, and alloy chemistry collectively govern the final microstructure and properties of Ti-6Al-4V-Cu fabricated via EB-PBF.

#### 3.6.1 Optical Microscopy

Optical microscopy was employed as an initial macrostructural characterization technique to evaluate the global solidification features of the fabricated specimens across the Y-Z build plane. The primary objective was to capture large-scale microstructural characteristics such as melt pool geometry, layer-to-layer overlap, and the continuity of the solidified tracks formed during the layer-wise EB-PBF process.

Particular emphasis was placed on identifying prior- $\beta$  grain morphology and its variation along the build direction, as these features are strongly governed by the local thermal gradients and repeated thermal cycling inherent to additive manufacturing [63]. The evolution of grain structure from the bottom to the top regions of the build provides direct evidence of changes in heat accumulation, cooling rate, and thermal stability during fabrication. In this context, optical microscopy enables a clear visualization of the transition from directional solidification features to more complex and heterogeneous grain arrangements influenced by process–thermal interactions.

In addition, optical imaging was used to assess structural anisotropy, which is a well-known characteristic of EB-PBF titanium alloys. This anisotropy originates from the strong directional heat flow associated with layer-by-layer deposition and results in elongated grain structures aligned preferentially along the build direction. Variations in melt pool overlap and track morphology also provide indirect information about process stability, energy input consistency, and potential local defects such as lack of fusion or irregular solidification zones [12,64].

Although optical microscopy is limited in resolution compared to electron-based techniques, it plays a crucial role as a bridge between process parameters and microstructural evolution. It enables rapid identification of representative regions, melt pool boundaries, and structural heterogeneities, which are subsequently selected for detailed high-resolution analysis using SEM and other advanced characterization methods. In this way, optical microscopy provides an essential first-level understanding of the hierarchical structure developed during EB-PBF processing of Ti-6Al-4V–Cu alloys.

### 3.6.2 X-ray Diffraction (XRD)

Phase identification and crystallographic analysis were carried out using X-ray diffraction (XRD) with Cu-K $\alpha$  radiation. The main goal was to identify the phase constitution of the as-built material and to understand how the  $\alpha$  and  $\beta$  phases of titanium evolve under the rapid solidification conditions and repeated thermal cycling typical of EB-PBF [33].

The analysis focused not only on the presence of the primary  $\alpha$ -Ti and  $\beta$ -Ti phases, but also on possible secondary phases introduced by Cu alloying. In particular, the formation of Ti<sub>2</sub>Cu intermetallic compounds was carefully investigated, as Cu has limited solubility in titanium and tends to segregate during solidification. Any additional diffraction peaks, peak shifts, or changes in intensity were used as indicators of phase formation, solute incorporation, or local chemical changes within the matrix [65].

Beyond simple phase identification, the diffraction patterns were also analyzed to understand changes in crystal structure caused by the processing conditions. Peak broadening was considered as an indication of reduced crystallite size and increased microstrain, both of which are commonly associated with rapid cooling rates and non-equilibrium solidification. Subtle shifts in peak positions were also examined, as they can suggest lattice distortion due to Cu atoms dissolving into the Ti matrix or residual stresses generated during the layer-wise thermal cycles.

Texture development was another important aspect of the analysis. Variations in relative peak intensities provided insight into preferred crystallographic orientations, which are often observed in additively manufactured titanium alloys due to directional heat flow and epitaxial grain growth. These effects are strongly influenced by the thermal gradients and solidification dynamics of EB-PBF, where repeated reheating can further modify the final phase arrangement and structural stability [20,66].

Overall, XRD provided essential information on the crystallographic state of the material and helped link processing conditions to phase evolution. When combined with microstructural observations, it confirmed the coexistence of  $\alpha$ -Ti, retained  $\beta$ -Ti, and Cu-related intermetallic phases, and highlighted the strong influence of EB-PBF thermal history on the final structural configuration of the alloy.

### 3.6.3 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) was used to investigate the microstructure at a much higher spatial resolution, allowing detailed examination of the hierarchical features formed across the Y–Z cross-section of the fabricated samples. This technique was essential for understanding how the microstructure evolves from the melt pool scale down to the grain and phase level under the complex thermal conditions of EB-PBF [67].

SEM imaging provided clear visualization of prior- $\beta$  grain structures, including both columnar and equiaxed regions, as well as the transition zones between them. These transitions are particularly important, as they reflect local variations in thermal gradient and cooling rate during layer-by-layer deposition. In areas where heat accumulation was more pronounced, elongated columnar grains aligned with the build direction were typically observed, while regions influenced by enhanced nucleation showed more equiaxed grain formation, indicating a shift in solidification behavior.

Special attention was also given to melt pool overlap regions, where successive thermal cycles repeatedly reheat previously solidified material. These areas often exhibit microstructural modifications such as grain coarsening, partial remelting at boundaries, and local changes in phase distribution [68]. The interaction between overlapping melt pools plays a key role in defining the final microstructural uniformity and contributes to the development of crystallographic texture throughout the build.

In addition, SEM analysis helped to identify the presence and distribution of secondary features such as fine  $\alpha$ -laths, intergranular precipitates, and Cu-enriched regions associated with local compositional fluctuations. These features are strongly influenced by non-equilibrium solidification and solute redistribution during processing. So, the SEM results provide direct evidence of the strong coupling between thermal history and microstructural evolution in EB-PBF. The observed grain morphology and phase distribution reflect the competition between epitaxial grain growth driven by directional heat flow and heterogeneous nucleation promoted by localized thermal and compositional variations, particularly in the presence of Cu alloying [17,69].

### 3.6.4 Energy Dispersive Spectroscopy (EDS)

Elemental distribution analysis was performed using Energy Dispersive Spectroscopy (EDS) to evaluate the compositional homogeneity and solute redistribution within the microstructure. The primary objective was to determine the effectiveness of in-situ alloying during EB-PBF processing and to identify any localized chemical heterogeneities induced by the rapid solidification conditions [70].

EDS elemental mapping and line scanning were employed to resolve spatial variations of the principal alloying elements across different microstructural regions. Particular attention was given to melt pool boundaries, interdendritic regions, and solidification bands, as these areas typically exhibit strong chemical gradients due to solute partitioning during solidification. These regions are especially critical in additive manufacturing, where repeated thermal cycling and rapid solidification promote non-equilibrium solidification conditions and localized enrichment phenomena [11,62].

The obtained compositional maps provide clear experimental evidence of solute redistribution mechanisms driven by the complex thermal conditions inherent to EB-PBF. These include melt pool convection, temperature-dependent diffusion, and solute rejection at the advancing solid–liquid interface. As solidification progresses, alloying elements with limited solubility are partially rejected into the remaining liquid, leading to localized compositional fluctuations that become “frozen in” due to rapid cooling rates [71].

In the case of Ti–6Al–4V–Cu systems, this behavior is particularly relevant, as Cu exhibits a strong tendency to segregate and form enriched regions, which can subsequently act as preferential sites for the formation of Ti<sub>2</sub>Cu intermetallic phases. The presence and spatial distribution of these enriched zones therefore provide direct insight into phase evolution pathways and precipitation behavior.

Overall, EDS analysis confirms that while a generally homogeneous alloying state is achieved through in-situ processing, localized microsegregation is still present as a natural consequence of rapid solidification and thermal cycling. These observations are essential for linking processing conditions with phase formation, microstructural evolution, and ultimately the resulting mechanical and functional properties of the alloy [72].

### 3.7 Nanohardness Testing

Nanohardness measurements were performed using an instrumented nanoindentation system to evaluate the local mechanical response of the additively manufactured Ti-6Al-4V and Ti-6Al-4V–Cu alloys. Unlike conventional microhardness techniques, nanoindentation enables mechanical characterization at the sub-micron scale, allowing direct correlation between mechanical response and individual microstructural features such as  $\alpha/\beta$  phases, Cu-enriched regions, and intermetallic precipitates formed during EB-PBF processing.

Indentations were carried out on carefully polished cross-sectional specimens using a Berkovich diamond indenter under controlled loading conditions. The loading–unloading profile and maximum indentation depth were selected to ensure that the indentation size remained significantly smaller than the characteristic microstructural length scale. This approach minimizes the influence of neighboring phases and ensures that the measured response is representative of local mechanical behavior rather than bulk-averaged properties [73].

The nanoindentation experiments were conducted at room temperature using a Hysitron TI-950 TriboIndenter system, which offers high-resolution force and displacement control with sensitivities of 0.1  $\mu\text{N}$  and 0.1 nm, respectively. The Berkovich indenter, with a nominal tip radius of approximately 20 nm, was calibrated prior to testing using fused quartz as a reference material to ensure accuracy and repeatability. A load-controlled mode was applied with a maximum load of 7000  $\mu\text{N}$ . To ensure statistical reliability and account for microstructural heterogeneity, at least nine indents were performed on each sample at different locations, including matrix regions and areas near melt pool boundaries [34].

The hardness and reduced elastic modulus were calculated from the load–displacement curves using the Oliver and Pharr method, which determines mechanical properties based on the unloading stiffness and the projected contact area at maximum indentation depth. This method is particularly suitable for heterogeneous additively manufactured materials, as it allows precise quantification of local mechanical variations associated with changes in phase composition and microstructure [11,74].

In the context of this study, nanoindentation plays a crucial role in linking microstructural evolution to mechanical performance. The presence of Cu-induced solid solution strengthening,  $\text{Ti}_2\text{Cu}$  precipitation, and microstructural refinement induced by EB-PBF thermal conditions are all expected to contribute to localized variations in hardness. Therefore, nanoindentation provides a direct experimental tool to capture these effects at the scale at which they occur, offering deeper insight into the strengthening mechanisms governing the Ti-6Al-4V–Cu system. So, the nanohardness results provide a sensitive and reliable assessment of how in-situ alloying and thermal history collectively influence the local mechanical response of additively manufactured titanium alloys [75].

### 3.8 Bioactivity Evaluation

The bioactivity of the fabricated specimens, with particular emphasis on hydroxyapatite (HA) formation and the influence of Cu addition on surface biological response, was evaluated through immersion in simulated body fluid (SBF). SBF is widely used to mimic the ionic concentration of human plasma and is considered a reliable in vitro medium for assessing the ability of biomaterials to induce apatite nucleation and growth on their surfaces [39].

Each sample was immersed in 20 mL of SBF solution and maintained under static conditions in an incubator (Mettler GmbH, Germany) at  $37 \pm 2^\circ\text{C}$  for 7 and 14 days, without light irradiation. These conditions were selected to closely replicate physiological temperature while avoiding external variables that could influence ion exchange kinetics or surface reactions. The chosen

immersion times were intended to capture both the early-stage nucleation behavior (7 days) and the more developed apatite layer formation (14 days), thereby enabling a time-dependent evaluation of surface bioactivity [76].

During immersion, surface reactions are governed by a sequence of processes including ion adsorption, nucleation of calcium phosphate clusters, and subsequent growth into a continuous hydroxyapatite layer. These mechanisms are strongly influenced by surface chemistry, roughness, phase composition, and the presence of alloying elements such as Cu, which can modify local electrochemical behavior and ion release dynamics.

After immersion, the specimens were carefully removed from the SBF solution, gently rinsed with distilled water to remove loosely attached salts, and dried under controlled conditions to preserve the integrity of the formed surface layers before characterization.

The surface morphology and elemental composition of the treated samples were analyzed using SEM combined with EDS. SEM was employed to identify morphological features associated with apatite nucleation and growth, while EDS provided quantitative elemental information, particularly regarding Ca, P, O, Ti, and Cu distribution across the surface [77].

To ensure statistical reliability and account for possible surface heterogeneity, EDS analyses were performed at five randomly selected locations on each sample surface. The average Ca/P atomic ratio was calculated and used as an indicator of hydroxyapatite formation, where values approaching the stoichiometric ratio of natural bone-like apatite further confirm enhanced bioactivity. This approach allows a systematic evaluation of how in-situ Cu addition and EB-PBF-induced surface characteristics influence the bioactive response of Ti-6Al-4V–Cu alloys, particularly in terms of apatite formation kinetics, surface reactivity, and potential suitability for biomedical implant applications [39,78].

## Chapter 4

### Results and Discussion

The present study investigates the influence of in-situ Cu alloying on the microstructural evolution, phase formation, and mechanical response of Ti-6Al-4V processed via EB-PBF. In contrast to process-parameter optimization approaches commonly reported in the literature, the present work maintains constant processing conditions to isolate the effect of alloy chemistry on solidification behavior [7]. This approach is consistent with the solidification-centered framework described in the reference AM literature, where grain morphology is governed by the coupled interaction between G, R, and solute redistribution effects.

To establish a complete process–structure–property correlation, a combination of complementary characterization techniques was employed. OM was used to quantify the overall grain morphology and to identify transitions in prior- $\beta$  grain structure induced by Cu addition [4,15]. Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy (SEM–EDS) provided local compositional analysis, enabling the identification of Cu segregation patterns and their relationship with melt pool solidification features. XRD was used to determine phase constitution and to detect the presence of Cu-related intermetallics and lattice distortion effects associated with solute incorporation [79]. Nanoindentation was employed to evaluate local mechanical response at the microstructural scale, allowing direct correlation between hardness variations and phase/morphology distribution. In addition, biological characterization was conducted to assess the functional implications of Cu addition, particularly in relation to its known antibacterial activity in Ti-based systems.

The combined results indicate that Cu plays an active role in modifying solidification thermodynamics rather than acting as a passive alloying addition. The primary effect is the introduction of solute-driven constitutional undercooling ahead of the solid–liquid interface, which modifies the local stability of the growing front and alters the balance between directional growth and nucleation. As a result, a pronounced change in grain morphology is observed, where the typical epitaxial columnar prior- $\beta$  structure of Ti-6Al-4V is significantly suppressed and replaced

by a predominantly equiaxed grain structure, despite unchanged EB-PBF processing conditions. These results confirm the coexistence of solid solution strengthening and precipitation phenomena within the same material system [11,78].

From a mechanical perspective, nanoindentation results show an overall increase in hardness in the Cu-containing alloy. This improvement is attributed to the combined contribution of solid solution strengthening, precipitation hardening from  $\text{Ti}_2\text{Cu}$  formation, and microstructural refinement associated with the CET [80]. Importantly, the spatial variation in hardness is consistent with local compositional heterogeneity identified by SEM-EDS, confirming a direct link between solute redistribution and local mechanical response.

Overall, the results confirm that Cu acts as a solute-driven control parameter capable of altering solidification pathways, phase evolution, and mechanical response under fixed EB-PBF thermal conditions. This directly supports the central hypothesis of this study and aligns with established solidification theory, where grain morphology is governed by the coupled effects of  $G$ ,  $R$ , and constitutional undercooling rather than process parameters alone [81].

#### 4.1 Microstructural Evolution Under EB-PBF Thermal Conditions

The microstructural comparison between the base Ti-6Al-4V alloy and the Cu-containing system reveals a fundamental shift in solidification mode, despite identical processing conditions. This indicates that the observed microstructural evolution is governed primarily by alloy thermodynamics rather than external thermal input.

In the reference Ti-6Al-4V alloy, the microstructure is dominated by elongated columnar prior- $\beta$  grains extending continuously across multiple deposited layers along the build direction. This morphology is a direct consequence of directional solidification under a persistent thermal gradient established between the molten pool and the previously solidified material, which acts as a heat sink. Under such conditions, epitaxial grain growth dominates, resulting in strong crystallographic texture and limited nucleation events at the solid-liquid interface [55,82].

Within these columnar prior- $\beta$  grains, the transformed microstructure consists of a fine  $\alpha + \beta$  lamellar (Widmanstätten) morphology. The relatively fine  $\alpha$ -lath spacing reflects the rapid thermal cycling inherent to EB-PBF, where repeated reheating of previously solidified layers leads to partial coarsening and stabilization of the lamellar structure rather than full martensitic transformation [80].

In contrast, the addition of Cu leads to a pronounced modification of the grain selection mechanism. The microstructure shifts toward predominantly equiaxed prior- $\beta$  grains with a broad size distribution. This transition indicates a breakdown of continuous epitaxial growth and the activation of widespread nucleation ahead of the solidification front [2].

Importantly, this transformation is not associated with any change in processing parameters such as beam power, scan strategy, or preheating temperature. Therefore, the change in morphology must be attributed to solute-driven modifications of the local solidification environment, rather than thermal reconfiguration of the process window.

In addition, the Cu-containing system exhibits a coarser  $\alpha + \beta$  lamellar structure compared to the base alloy. This suggests a modification in effective thermal conditions at the microscale, likely related to altered local solidification kinetics and extended thermal exposure due to solute redistribution effects in the melt pool [83]. The presence of Cu also influences heat flow and solidification front stability, indirectly modifying cooling pathways and phase transformation kinetics.

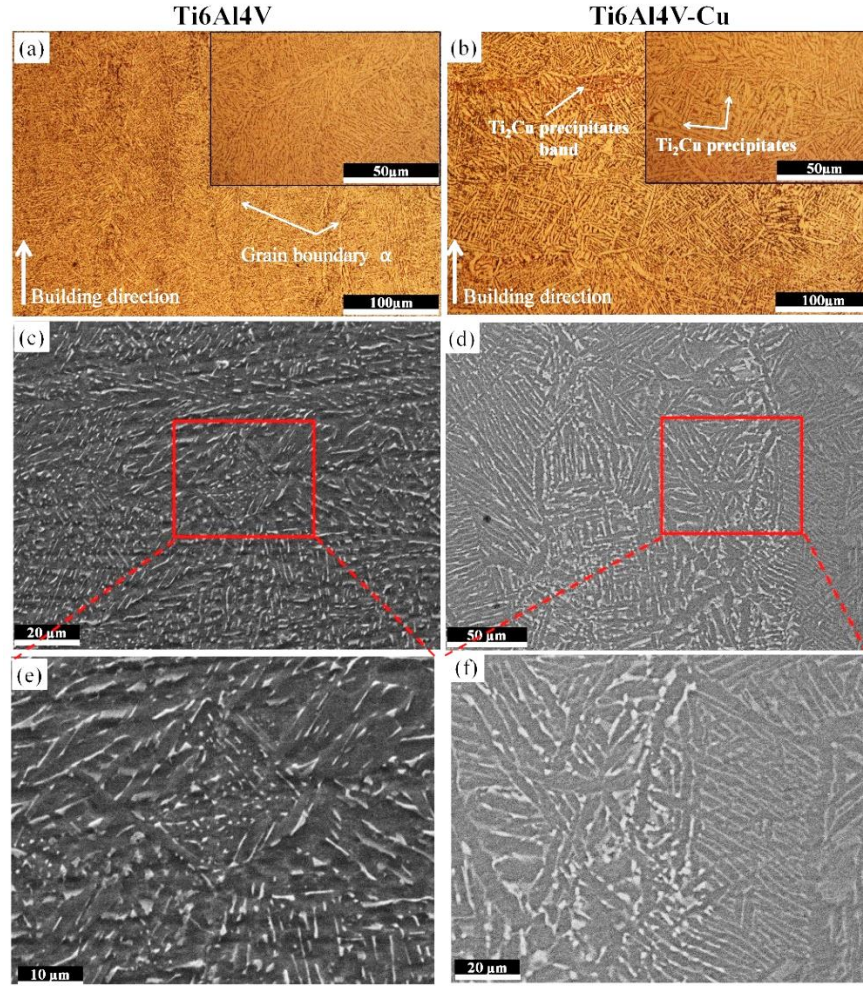


Fig. 34. OM and SEM of a, c, e Ti6Al4V and b, d, f Ti6Al4V-Cu samples. [1]

As shown in Figure 34, the transition from columnar to equiaxed solidification observed in the Cu-containing alloy can be fundamentally explained through the concept of constitutional supercooling, which governs interface stability during alloy solidification.

During solidification, Cu exhibits a strong partitioning tendency due to its limited solubility in titanium. As the solid-liquid interface advances, Cu is rejected into the remaining liquid, leading to the formation of a solute-enriched boundary layer ahead of the interface. This enrichment locally depresses the liquidus temperature, creating a region where the actual temperature is below the equilibrium solidification temperature, thereby establishing a constitutionally supercooled zone [1].

This instability reduces the morphological stability of the solidification front and increases the probability of heterogeneous nucleation ahead of the interface. The intensity of this effect is commonly described by the growth restriction factor ( $Q$ ), which captures the combined influence of solute partitioning, liquidus slope, and alloy concentration [83]. A higher  $Q$  value corresponds to stronger growth restriction and increased nucleation density.

In the Ti–Cu system, the high partitioning behavior of Cu significantly increases  $Q$  compared to the base Ti-6Al-4V alloy system. As a result, the solute field ahead of the solidification front becomes sufficiently enriched to destabilize epitaxial growth and promote independent nucleation events.

Under EB-PBF conditions, this solute-driven mechanism is further amplified by the intrinsic thermal characteristics of the process. The reduced thermal gradient, resulting from elevated preheating, limits directional heat extraction and weakens interface stability. Simultaneously, the solidification rate remains relatively high due to rapid beam scanning, leading to a combined reduction in the effective  $G/R$  ratio [6].

The coupling between a reduced  $G/R$  ratio and enhanced constitutional supercooling creates a thermodynamic regime favorable for the breakdown of columnar growth and the activation of equiaxed nucleation throughout the melt pool volume. This marks a transition from growth-controlled to nucleation-controlled solidification [84].

Consequently, the observed columnar-to-equiaxed transition is not solely a thermal phenomenon but the result of a coupled thermo-solutal instability, where Cu acts as a driving force that modifies interface stability under otherwise unchanged processing conditions.

This result is significant because it demonstrates that in EB-PBF, microstructural evolution can be actively tuned through alloy chemistry, enabling structural control without modifying process parameters. Such a mechanism provides a powerful route for microstructural engineering in additively manufactured titanium alloys, particularly where isotropy and property uniformity are required.

## 4.2 Phase Evolution and Precipitation Behavior

Although the Ti-6Al-4V –Cu alloy exhibits overall chemical homogeneity at the macroscopic scale, detailed microstructural and compositional analyses reveal the presence of localized Cu-enriched regions distributed throughout the build. These regions are commonly observed as narrow bands or interdendritic zones aligned parallel to the deposited layers, indicating a direct relationship between solute redistribution, melt pool geometry, and the layer-wise thermal history inherent to Electron Beam Powder Bed Fusion [3].

The formation of these Cu-rich regions originates from the limited solubility of Cu in the solid Ti matrix during rapid solidification. As the solid–liquid interface advances, Cu is rejected into the remaining liquid phase due to partitioning effects, resulting in progressive solute enrichment ahead of the interface [85]. Under the non-equilibrium conditions characteristic of additive

manufacturing, diffusion in the solid state is insufficient to fully homogenize the composition, leading to the retention of local concentration gradients after solidification.

This segregation behavior is strongly coupled with melt pool dynamics. In EB-PBF, the melt pool is not static but continuously influenced by thermal convection, Marangoni-driven surface tension flow, recoil pressure effects, and repeated reheating from subsequent layers. These phenomena govern the transport of liquid metal and dissolved solute within the melt pool before solidification occurs. Consequently, Cu redistribution becomes highly dependent on local thermal conditions, melt pool lifetime, and fluid flow behavior [2,41].

Compared with Laser Powder Bed Fusion, the larger and thermally more stable melt pools in EB-PBF promote improved elemental mixing and reduced compositional fluctuation at the macro-scale. The elevated preheating temperatures characteristic of EB-PBF also reduce cooling rates and extend the liquid lifetime, allowing greater diffusion and redistribution of Cu throughout the molten region. However, despite this enhanced homogenization capability, complete elimination of microsegregation is not achieved due to the inherently rapid and directional nature of solidification [11].

The observed layer-aligned Cu-rich bands additionally indicate the influence of cyclic thermal exposure during layer-by-layer fabrication. Each deposited layer partially remelts and reheats the underlying material, producing repeated thermal cycling that modifies local diffusion behavior and redistributes segregated solute. This repeated remelting–solidification sequence contributes to the development of heterogeneous microstructural regions associated with previous melt pool boundaries.

From a solidification perspective, these observations confirm that the EB-PBF process creates a highly transient thermodynamic environment in which thermal gradients, melt pool convection, and solute partitioning interact simultaneously. The resulting microstructure therefore reflects not only equilibrium alloy chemistry, but also the kinetic limitations imposed by rapid solidification and cyclic reheating [12,86]. Importantly, the presence of localized Cu enrichment also supports the mechanisms proposed earlier regarding constitutional undercooling and grain morphology modification. The accumulation of Cu ahead of the advancing solidification front locally reduces the liquidus temperature and destabilizes directional growth, thereby increasing nucleation probability and promoting equiaxed grain formation.

Overall, the results demonstrate that melt pool dynamics play a central role in determining solute redistribution during in-situ alloying. While EB-PBF provides improved thermal stability and enhanced mixing compared with laser-based systems, micro-scale segregation remains an intrinsic feature of rapidly solidified Ti–Cu alloys. Consequently, achieving optimal chemical homogeneity requires careful control of both alloy composition and thermal processing conditions.

Fig. 35. a-c presents the elemental distribution analysis derived from EDS mapping of the Ti5Al3V6Cu microstructure, aimed at examining the partitioning of elements between the matrix phases and the Ti2Cu secondary phase. The copper distribution within the matrix, particularly in the alpha phase, is observed to be homogeneous, as illustrated in Figure 2, with no evident regions exhibiting copper enrichment [16]. This uniformity is attributed to the extensive melt pool

generated during the EB-PBF process, which facilitates the melting of copper powders and promotes thorough mixing of the resultant melt with molten titanium. Generally, the formation of  $\text{Ti}_2\text{Cu}$  precipitates occurs either via eutectoid decomposition of the beta phase or through precipitation from the supersaturated alpha phase, a process driven by the diminished solubility of copper in the alpha phase at reduced temperatures [25].

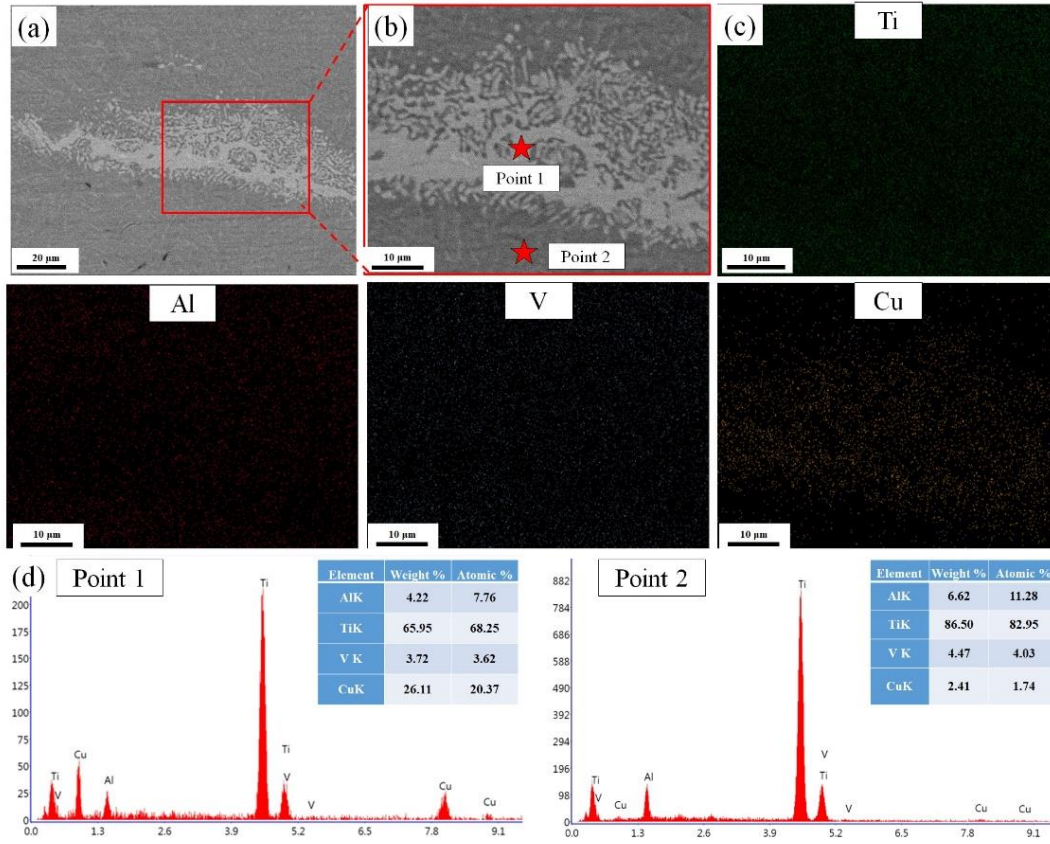


Fig. 35. EDS mapping of Ti6Al4V-Cu sample.

The redistribution of Cu during solidification has a direct influence on phase evolution and precipitation behavior within the Ti-6Al-4V–Cu alloy. Owing to the limited equilibrium solubility of Cu in titanium, the local enrichment of Cu during solidification promotes the formation of secondary phases within the microstructure. Microstructural observations reveal the presence of dispersed precipitates distributed throughout the  $\alpha + \beta$  matrix, particularly within regions associated with Cu-rich segregation bands [87].

EDS analysis confirms that these precipitates are enriched in Cu and are primarily associated with the formation of  $\text{Ti}_2\text{Cu}$  intermetallic phases. This observation is consistent with thermodynamic predictions for Ti–Cu systems and agrees with previous studies reporting  $\text{Ti}_2\text{Cu}$  precipitation in additively manufactured Ti–Cu alloys. The chemical compositions of different points, indicated in Figure 35, were analyzed using EDS. The precipitates exhibit multiple morphologies, including fine dispersed particles, irregular blocky features, and elongated intermetallic regions. This morphological diversity reflects the highly non-equilibrium nature of the EB-PBF process, where

local cooling conditions vary significantly throughout the melt pool and between successive layers. Variations in local thermal gradients, cooling rates, and reheating cycles influence nucleation and growth kinetics, leading to heterogeneous precipitation behavior across the build.

The repeated thermal cycling intrinsic to EB-PBF further contributes to phase evolution. During layer-wise fabrication, previously solidified regions are repeatedly reheated to elevated temperatures below the melting point. These cyclic reheating events effectively introduce localized annealing and ageing phenomena, promoting diffusion-driven precipitation and phase transformation processes. As a result, the final microstructure is not solely determined by primary solidification, but also by subsequent solid-state thermal evolution occurring throughout the build process.

Within the Cu-enriched regions, the increased local concentration of Cu provides favorable thermodynamic conditions for  $\text{Ti}_2\text{Cu}$  precipitation. Consequently, a higher density of precipitates is typically observed near melt pool boundaries and interdendritic regions where segregation is most pronounced. This demonstrates that precipitation behavior is strongly linked to local compositional heterogeneity generated during solidification [25,88].

As seen in Figure 36, XRD analysis further supports these observations by confirming the presence of  $\alpha$ -Ti, retained  $\beta$  phases, and  $\text{Ti}_2\text{Cu}$  intermetallic compounds within the alloy. In addition, a slight shift in the  $\alpha$ -phase diffraction peaks toward higher diffraction angles is observed in the Cu-containing alloy. This shift indicates a reduction in lattice spacing associated with the substitutional incorporation of Cu atoms into the Ti matrix, providing evidence of partial solid solution formation in addition to intermetallic precipitation.

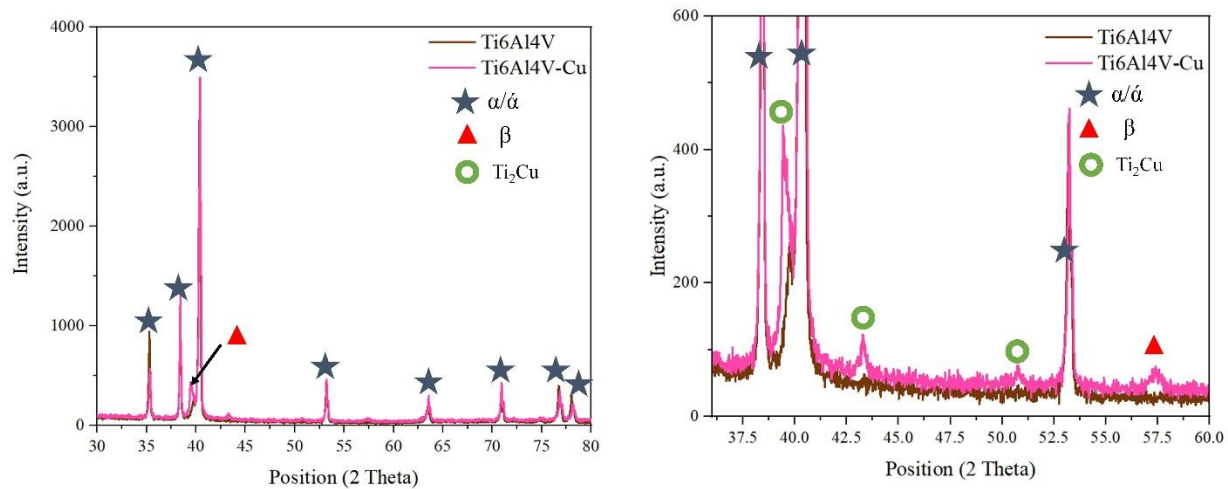


Fig. 36. XRD patterns of as-built Ti6Al4V and Ti6Al4V-Cu produced in this work.

The coexistence of solid solution strengthening and precipitation strengthening mechanisms is particularly important for understanding the mechanical response of the alloy. Cu atoms dissolved within the Ti lattice introduce local lattice distortions that impede dislocation movement, while  $\text{Ti}_2\text{Cu}$  precipitates act as strong obstacles to plastic deformation. Together, these mechanisms contribute significantly to the enhanced hardness observed in the Cu-modified alloy.

From a broader microstructural perspective, the phase evolution behavior demonstrates the strong coupling between thermal history and alloy chemistry in EB-PBF-processed systems. The final phase constitution is governed not only by equilibrium thermodynamics, but also by rapid solidification kinetics, solute partitioning, and repeated thermal cycling. Consequently, the Ti-6Al-4V –Cu alloy develops a complex hierarchical microstructure consisting of  $\alpha + \beta$  phases, Cu-enriched regions, and Ti<sub>2</sub>Cu precipitates distributed across multiple length scales [89].

Overall, the results confirm that Cu addition fundamentally alters phase evolution pathways during EB-PBF processing. While Cu promotes desirable strengthening effects through solid solution and precipitation mechanisms, its limited solubility also introduces microstructural heterogeneity that must be carefully controlled to achieve balanced mechanical performance and structural stability.

### 4.3 Mechanical Properties

Nanohardness measurements reveal a clear enhancement in the mechanical response of the Ti-6Al-4V –Cu alloy compared with the base Ti-6Al-4V material processed under identical EB-PBF conditions. The increase in hardness demonstrates that the introduction of Cu significantly modifies strengthening behavior through multiple interacting microstructural mechanisms.

Interestingly, this increase in hardness occurs despite the relatively coarser  $\alpha + \beta$  morphology observed in the Cu-containing alloy [5]. In conventional metallic systems, microstructural coarsening is typically associated with reduced hardness due to the decrease in grain boundary density. However, the present results indicate that strengthening contributions arising from alloy chemistry and phase evolution outweigh the softening effect associated with coarsened lamellar structures.

One of the primary strengthening contributions originates from solid solution strengthening. A portion of the Cu atoms becomes dissolved within the Ti matrix during solidification and subsequent thermal cycling. Because Cu atoms possess a different atomic radius and elastic modulus compared with Ti, their incorporation generates localized lattice distortions within the crystal structure. These distortions increase resistance to dislocation motion and thereby enhance hardness [41,90].

A second major contribution arises from precipitation strengthening associated with the formation of Ti<sub>2</sub>Cu intermetallic phases. The dispersed intermetallic precipitates observed throughout the microstructure act as physical barriers to dislocation movement. The interaction between dislocations and these hard precipitates increases the stress required for plastic deformation, contributing significantly to the overall hardness increase.

Figure 37 presents that the modified grain morphology also influences mechanical behavior. The transition from elongated columnar grains toward a more equiaxed structure reduces directional dependence in deformation behavior and improves microstructural isotropy. In conventional additively manufactured Ti-6Al-4V, the strong columnar prior- $\beta$  grain structure promotes anisotropic mechanical response due to directional epitaxial growth. In contrast, the equiaxed

morphology observed in the Cu-containing alloy promotes more homogeneous stress distribution during deformation [37].

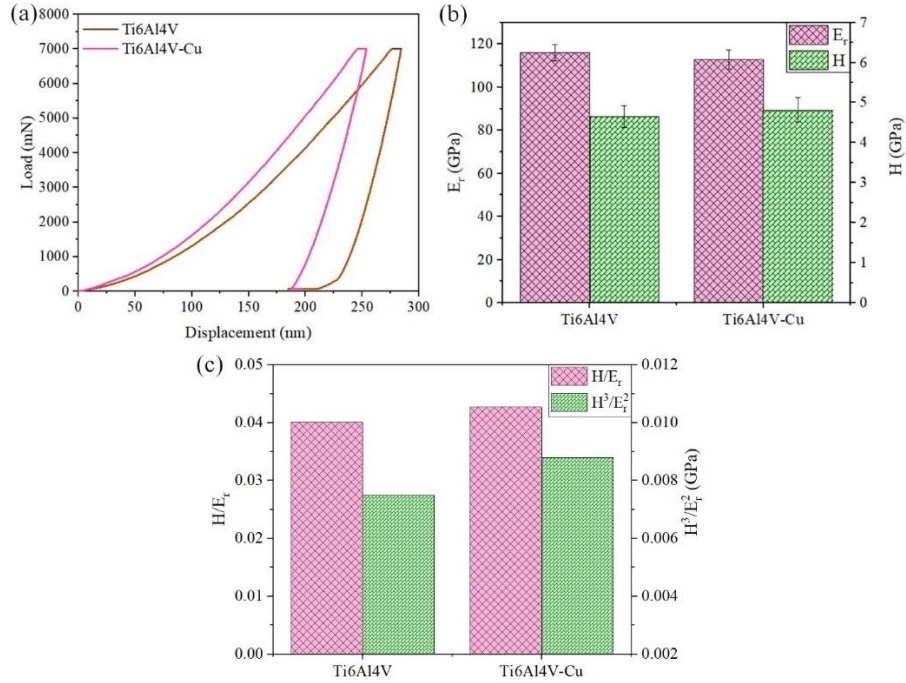


Fig. 37. (a) Representative load–displacement nanoindentation curves, (b)  $H$  and  $E_r$  values, (c) the  $H/E_r$  and  $H^3/E_r^2$  ratios. [37]

Spatial variations in hardness are observed across different regions of the build, particularly near melt pool boundaries and Cu-enriched zones. These local variations correlate closely with compositional heterogeneity and precipitate distribution, confirming the strong relationship between local microstructure and mechanical response. Regions containing higher concentrations of  $Ti_2Cu$  precipitates generally exhibit increased hardness due to enhanced precipitation strengthening [91].

The layer-wise thermal history of EB-PBF additionally contributes to hardness evolution. Repeated reheating cycles during fabrication can promote partial tempering, diffusion, and secondary precipitation reactions within previously solidified layers [7]. These thermal effects produce local variations in phase composition and precipitate morphology, further influencing the hardness distribution throughout the build.

Compared with conventionally processed Ti-6Al-4V, the present alloy system therefore exhibits a more complex strengthening behavior governed by the combined interaction of:

- solid solution strengthening,
- precipitation hardening,
- grain morphology modification,
- thermal cycling effects, and
- local compositional heterogeneity.

The results also demonstrate that hardness cannot be interpreted solely in terms of grain size or  $\alpha$ -lath thickness in additively manufactured alloys. Instead, mechanical performance is strongly dependent on the coupled interaction between thermal conditions, alloy chemistry, and non-equilibrium phase evolution.

Overall, the mechanical response confirms that Cu acts as an effective strengthening addition in EB-PBF-processed Ti-6Al-4V. The combination of enhanced hardness, modified grain morphology, and improved isotropy highlights the potential of in-situ alloying as a strategy for engineering high-performance titanium alloys through direct control of solidification behavior and microstructural evolution [92].

#### 4.4 Integrated Structure–Property Relationship

The results obtained in this study demonstrate that the microstructural evolution and resulting properties of Ti-6Al-4V–Cu processed by EB-PBF are governed by a strongly coupled interaction between alloy chemistry, thermal conditions, melt pool dynamics, and solidification kinetics. Rather than acting independently, these factors collectively determine the final process–structure–property relationship of the alloy system [4].

At the process level, the EB-PBF environment provides a unique thermal regime characterized by elevated powder bed preheating, reduced thermal gradients, vacuum processing conditions, and relatively stable melt pools. Compared with laser-based additive manufacturing systems, these conditions significantly modify heat transfer behavior, reduce cooling rates, and promote enhanced thermal stability throughout the build.

These thermal characteristics directly influence the solidification pathway of the alloy. The reduced thermal gradient lowers the stability of directional solidification and weakens the dominance of epitaxial columnar grain growth. Simultaneously, the addition of Cu introduces strong solute-driven effects through constitutional undercooling [9,93]. During solidification, Cu segregation ahead of the solid–liquid interface lowers the local liquidus temperature and increases the nucleation driving force, promoting heterogeneous nucleation within the liquid.

The combined effect of reduced thermal gradients and Cu-induced constitutional undercooling produces conditions favorable for the CET. As a result, the conventional elongated columnar prior- $\beta$  grain structure characteristic of additively manufactured Ti-6Al-4V is replaced by a substantially more equiaxed grain morphology. This transition represents one of the most important microstructural outcomes of the present work because it directly influences anisotropy, texture development, and mechanical response [25].

At the same time, the non-equilibrium solidification conditions inherent to EB-PBF generate localized solute redistribution and microsegregation. Cu enrichment within interdendritic and melt pool boundary regions promotes the formation of  $\text{Ti}_2\text{Cu}$  intermetallic phases during solidification and subsequent thermal cycling. Consequently, the final microstructure consists of multiple interacting constituents, including:

- equiaxed prior- $\beta$  grains,
- $\alpha + \beta$  lamellar phases,
- Cu-enriched segregation regions, and
- dispersed  $\text{Ti}_2\text{Cu}$  precipitates.

This hierarchical microstructure gives rise to the observed mechanical behavior. Solid solution strengthening from dissolved Cu atoms, combined with precipitation strengthening from  $\text{Ti}_2\text{Cu}$  intermetallics, increases hardness despite the coarsening of  $\alpha$ -lath morphology. Furthermore, the equiaxed grain structure reduces directional anisotropy and promotes more uniform mechanical response throughout the material [94].

Importantly, the results demonstrate that microstructural engineering in additive manufacturing cannot be achieved solely through process parameter optimization. Instead, alloy composition itself can serve as an active mechanism for controlling solidification behavior and phase evolution. In this study, Cu functions not merely as an alloying addition, but as a thermodynamic and kinetic modifier capable of altering nucleation behavior, grain growth stability, and precipitation pathways under fixed EB-PBF conditions. The integrated framework established in this work, therefore, highlights the importance of simultaneously considering:

- process parameters,
- thermal field evolution,
- melt pool behavior,
- solute redistribution,
- solidification kinetics, and
- phase transformation

when designing additively manufactured alloys [40].

From a broader perspective, the findings demonstrate the potential of in-situ alloying as an advanced strategy for process-driven microstructural design in additive manufacturing. By coupling controlled alloy chemistry with tailored thermal conditions, it becomes possible to engineer titanium alloys with improved isotropy, enhanced mechanical performance, and multifunctional behavior directly during fabrication, thereby reducing reliance on extensive post-processing treatments.

Overall, this study establishes a comprehensive process–thermal–microstructure–property relationship for Ti-6Al-4V–Cu processed via EB-PBF and provides important insight into the fundamental mechanisms governing alloy development under non-equilibrium additive manufacturing conditions [91].

## 4.5 Biocompatibility and Bioactivity Response

In addition to its influence on solidification behavior and mechanical performance, Cu incorporation in Ti-6Al-4V processed via EB-PBF introduces an additional functional dimension related to biological response. This reflects the dual role of Cu as both a microstructural modifier, through solute-driven effects during solidification, and a biofunctional element associated with antibacterial activity in Ti-based biomedical alloys.

To evaluate in vitro bioactivity, SBF immersion tests were conducted for 14 days on both Ti-6Al-4V and Ti-6Al-4V –Cu samples. The formation of hydroxyapatite (HA)-like layers on the material surface was used as an indicator of bioactivity and bone-bonding capability, as widely established in the literature. A faster and more uniform apatite formation is generally associated with enhanced osteoconductive potential [6,43].

Figure 38 illustrates the SEM surface morphologies of both materials after SBF immersion. Both samples exhibit the formation of flake-like calcium phosphate deposits covering the surface after 14 days. However, the Cu-containing alloy shows a more continuous and denser apatite layer compared to the base alloy, suggesting enhanced surface reactivity and accelerated nucleation kinetics.

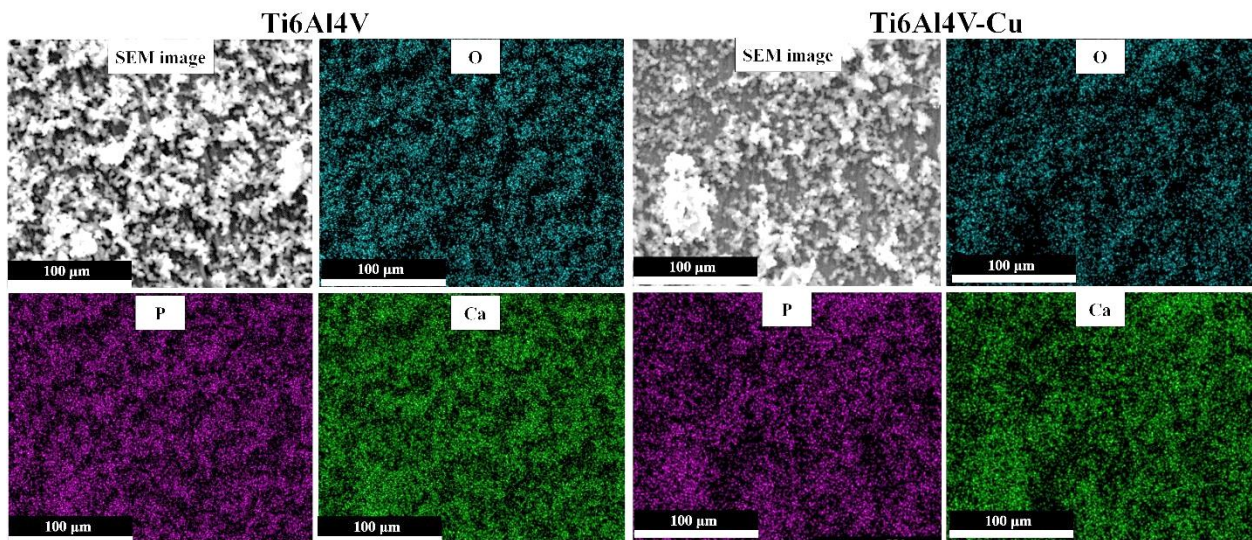


Fig. 38. SEM -EDX images of Ti6Al4V and Ti6Al4V-Cu samples after immersion in SBF for 14 (D14) days at 37 °C.

The improved apatite formation in the Cu-modified alloy can be linked to its microstructural state induced by EB-PBF processing and solute effects. In particular, Cu-induced constitutional undercooling during solidification leads to modified grain morphology and increased density of microstructural interfaces, which act as preferential nucleation sites for calcium phosphate precipitation. Additionally, lattice distortions caused by Cu in solid solution may increase surface energy heterogeneity, further promoting heterogeneous nucleation in SBF environments.

EDS analysis confirms the presence of calcium (Ca) and phosphorus (P) in the deposited layers, with elemental ratios consistent with hydroxyapatite formation. The Ca/P ratio falls within the

range typically reported for biologically active apatite-like phases, confirming the bio-relevance of the observed surface deposits [95]. From a mechanistic perspective, the enhanced bioactivity of the Cu-containing alloy results from a synergistic interaction between microstructural refinement, solute redistribution, and surface chemistry modification induced during EB-PBF processing. While the thermal conditions of EB-PBF provide a stable baseline for surface formation, Cu addition further enhances surface reactivity and nucleation behavior.

Ultimately, the results demonstrate that Cu addition does not compromise bioactivity; instead, it enhances hydroxyapatite formation while simultaneously providing antibacterial functionality reported in Ti–Cu systems. This confirms that Ti-6Al-4V –Cu produced via EB-PBF exhibits a combined structural and biological performance advantage, making it a strong candidate for biomedical implant applications [41,95].

## Chapter 5

### Conclusion and Future Perspectives

This study investigated the influence of in-situ Cu alloying on the microstructural evolution, phase formation, mechanical performance, and biofunctional behavior of Ti-6Al-4V processed via Electron Beam Powder Bed Fusion (EB-PBF). The work was motivated by the limited understanding of the coupled interaction between alloy chemistry and the unique thermal conditions of EB-PBF, particularly regarding the role of Cu in controlling solidification behavior and promoting microstructural refinement.

The results demonstrate that the combination of EB-PBF processing and Cu addition fundamentally modifies the solidification pathway of Ti-6Al-4V. Owing to the reduced thermal gradients inherent to EB-PBF and the strong solute-partitioning behavior of Cu, constitutional undercooling develops ahead of the advancing solidification front, promoting heterogeneous nucleation and suppressing epitaxial grain growth. Consequently, the conventional columnar prior- $\beta$  grain structure characteristic of additively manufactured Ti-6Al-4V is replaced by a predominantly equiaxed microstructure. This observation confirms that grain morphology in EB-PBF can be effectively controlled through alloy chemistry in addition to process parameter optimization.

Microstructural characterization further revealed that although the alloy exhibited good overall chemical homogeneity, localized Cu-enriched regions developed during solidification. These regions were primarily associated with layer-wise segregation phenomena resulting from solute rejection into the remaining liquid during solidification. The complex thermal history of EB-PBF, characterized by repeated heating and cooling cycles, contributed to the formation of  $\text{Ti}_2\text{Cu}$  intermetallic precipitates with varying morphologies and spatial distributions throughout the microstructure.

Phase analysis confirmed the coexistence of  $\alpha$  and  $\beta$  phases together with  $\text{Ti}_2\text{Cu}$  precipitates. Furthermore, evidence of Cu incorporation into the titanium matrix indicated that both solid-solution strengthening and precipitation strengthening mechanisms were active. The formation of

Ti<sub>2</sub>Cu phases and the redistribution of Cu during solidification played a significant role in determining the final microstructural state and mechanical response of the alloy.

Mechanical characterization demonstrated a clear increase in nanohardness for the Cu-containing alloy compared with the base Ti-6Al-4V material. Despite the relatively coarser  $\alpha + \beta$  lamellar morphology observed after Cu addition, hardness increased due to the combined contributions of solid-solution strengthening, Ti<sub>2</sub>Cu precipitation hardening, modified grain morphology, and the thermal cycling effects inherent to EB-PBF processing. The transition toward a more equiaxed grain structure additionally reduced microstructural anisotropy and promoted a more homogeneous deformation response.

Bioactivity evaluation in SBF demonstrated successful hydroxyapatite formation on both alloys, confirming their suitability for biomedical applications. The Cu-modified alloy exhibited a dense and continuous apatite layer after immersion, indicating that Cu addition does not compromise biological performance.

From a broader scientific perspective, this work addresses several of the knowledge gaps identified in the literature regarding Ti-6Al-4V –Cu systems processed by EB-PBF. The study provides evidence that Cu-induced constitutional undercooling, when coupled with the reduced thermal gradients of EB-PBF, serves as an effective mechanism for promoting the CET. Furthermore, the results establish a direct relationship between processing conditions, thermal behavior, solute redistribution, phase evolution, microstructural development, and resulting properties.

Overall, the findings demonstrate that in-situ alloying represents a powerful strategy for microstructural engineering in additive manufacturing. By exploiting the synergistic interaction between EB-PBF thermal conditions and Cu-induced solidification effects, it is possible to tailor grain morphology, phase constitution, mechanical performance, and biological response without altering the fundamental processing route. The knowledge generated in this study contributes to the development of next-generation titanium alloys with improved isotropy, enhanced functionality, and greater suitability for advanced biomedical and engineering applications.

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