

A review on enhancing near- α Ti alloys: exploring sintering additives in conjunction with CP-Ti

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Abstract. This review explores sintering additives' vital role in near-alpha titanium alloy production from commercially pure titanium, meeting demand for lightweight, high-strength materials. It emphasizes understanding the nuanced relationship between additives to optimize microstructures and enhance alloy performance. Beginning with the significance of near-alpha titanium alloys, it discusses the properties of commercially pure titanium and its limitations in high-performance applications. The review details the sintering process's crucial role, including its impact on resulting properties. Additionally, it examines various sintering additives, their roles in alloying, and their effects on microstructure and mechanical properties. Discussions on challenges, trends, future prospects, and existing literature augment the analysis.

1 Introduction

Near-alpha (Near- α) titanium (Ti) alloys are highly valued for their exceptional strength, low density, and corrosion resistance, making them well-suited for a diverse range of applications in industries such as automotive, aerospace, and biomedical. [1]. Near- α Ti alloys have exceptional creep resistance and durability at high temperatures, making them very suitable for use in settings with extreme temperatures [2]. These alloys primarily consist of the α -phase of Ti, characterized by a stable crystal structure with a hexagonal close-packed arrangement at room and moderate temperatures, combined with about 5-10 % of beta (β) phase contributing to their inherent strength and hardness [3, 4]. The β -phase is introduced by 1 – 2 wt.% of β -stabilizers [5, 6]. Moreover, near- α Ti alloys offer a superior strength-to-weight ratio, enabling the creation of lightweight components while maintaining structural integrity, a crucial advantage in aerospace applications for improved fuel efficiency and performance even at temperatures as high as 540 °C [7, 8]. In the aerospace sector, near- α Ti alloys have a long-standing history of use in advanced aircraft parts, including airframes, landing gear, and engine components, owing to their outstanding properties [9, 10]. However,

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these alloys are not limited to aerospace and find applications in medical implants, athletic products, and automotive components, demonstrating their versatility across various industries [11, 12].

Several near- α Ti alloys were fabricated and utilized in various applications at high temperatures, particularly for engines of aircraft. Meetham et al. [13] highlighted the use of the Ti-11Sn-1Mo-5Zr-2.5Al-0.25Si (IMI 679 alloy) in 1958 for the design of the RR Spey engine's discs and blades. Subsequently, Ti-6Al-5Zr-0.5Mo-0.25Si (IMI 685 alloy) was employed in 1964, offering higher fracture toughness, improved creep resistance, and good weldability. The alloy (IMI 685) found application in the RR Adour engine for Jaguar and Hawk aircraft. According to Boyer et al. [8], the Boeing 757 compressor design was developed using Ti-5.5Al-3.5Sn-3Zr-1Nb-0.25Mo-0.3Si (IMI 829) in the early 1980s, featuring enhanced resistance to creep. The near- α Ti alloy demonstrated remarkable thermal stability, functioning efficiently at temperatures above 500°C. Subsequently, in 1986, the high-pressure disc construction of the EJ200 engine was upgraded to use Ti-5.8Al-4Sn-3.5Zr-0.7Nb-0.5Mo-0.35Si-0.06C (IMI 834 alloy), an alloy that is stronger and can operate at higher temperature [14].

Despite the successful near- α Ti alloys' employment in producing aero-engines compressor parts, they are susceptible to mechanical deterioration at working temperatures over 600°C for extended periods. This is caused by brittle layer formation on the alloy surfaces [15]. In order to reduce the impact of these effects, it is usual practice to apply oxidation-resistant coatings to safeguard the components. Nevertheless, the usefulness of these materials is limited by the occurrence of fractures that form either during their application or as a result of cyclic oxidation. These cracks are a result of differences in strain between the coating and the underlying alloy [16]. As temperatures fluctuate, differences in thermal expansion coefficients between the oxide layer and the base material create stresses that can initiate cracks. According to Zhao et al. [17], such issues are particularly prominent in near-alpha titanium alloys, where subsurface fatigue crack initiation is observed under high-temperature fatigue conditions. These cracks can propagate during cyclic oxidation, undermining the protective properties of the coating. Moreover, the study emphasizes that fatigue behavior at elevated temperatures is affected by oxidation, although the oxide layer formed at moderate temperatures (like 450°C) may be thin. However, prolonged exposure to higher temperatures above 600°C can exacerbate oxidation, leading to the development of surface and subsurface cracks that compromise material integrity. This underscores the importance of oxidation-resistant coatings in mitigating these effects, albeit with the challenge of managing strain differences between the coating and substrate. Extensive research has been conducted to further enhance the oxidation resistance of near- α Ti [18-20].

Recent investigations have been devoted to the advancement of near- α Ti alloys through advanced processing techniques, alloy compositions, and microstructural refinements [3, 21-24]. **Fig. 1** depicts the evaluation of the elastic modulus and ultimate tensile strength (UTS) of near- α Ti alloys and other forms of Ti alloys. It is observed that near- α Ti has a good combination of elastic modulus and UTS. Sintering, a pivotal method, allows precise manipulation of alloy properties and performance by incorporating additives [25, 26]. This process significantly influences the microstructure, mechanical characteristics, and overall performance of near- α Ti alloys by promoting densification, regulating grain size, and enhancing the homogeneity of alloying elements [26, 27]. Researchers [17, 28, 29] have explored alloy design strategies to enhance the mechanical, heat, and corrosion resistance properties of near- α Ti alloys. These are achieved by exploring different sintering techniques,

optimizing sintering parameters, using different alloying elements as reinforcements, varying the wt.% of reinforcements, and employing post-sintering treatments.

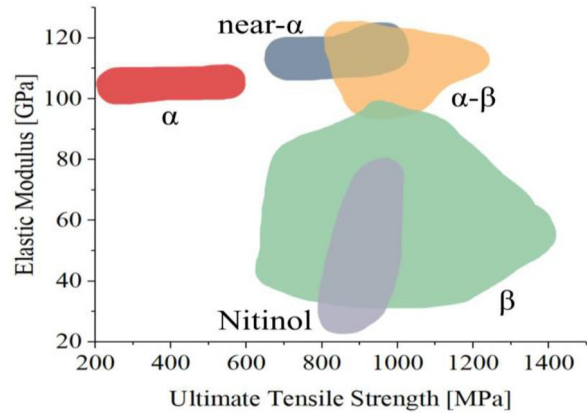


Fig. 1. Strength vs elastic modulus of near- α Ti to other Ti alloys [30].

The use of commercially pure (CP) Ti as a base material for near- α Ti alloys is pivotal for enhancing material properties through alloying elements' addition [31]. Commercially pure titanium possesses several key attributes that make it highly desirable: it has a remarkable strength-to-weight ratio that renders it highly suitable for applications where reduction in weight is of utmost importance, such as in aircraft, automotive, and sporting goods industries [32]. Additionally, its exceptional corrosion resistance surpasses that of stainless steel, making it suitable for maritime, chemical processing, and biomedical use [33-35]. The biocompatibility of Ti allows for extensive medical and dental implant applications due to its inert properties and ease of integration with biological tissues [33]. Titanium also exhibits thermal stability and can withstand extreme temperatures, making it suitable for aerospace and high-temperature industrial applications [34]. Despite these advantages, CP-Ti has limitations such as low to medium strength, lower modulus of elasticity compared to steel, higher cost, and limited wear resistance [10, 36]. Nonetheless, CP-Ti serves as a critical component in near- α Ti alloy development by providing a stable matrix for alloying additions, enhancing mechanical properties like strength and ductility. Furthermore, CP-Ti allows for the customization of alloy compositions to meet specific performance requirements through various processing techniques, including powder metallurgy and casting. Four grades of CP-Ti are classified by the American Society for Testing and Materials (ASTM) based on their oxygen content, as shown in Table 1. The oxygen levels significantly impact the mechanical properties and strength of these grades, with higher oxygen content resulting in increased strength but slightly reduced ductility. For example, Grade 1 has the lowest oxygen content, providing excellent corrosion resistance but lower strength, while Grade 4, with the highest oxygen level, offers superior strength. Overall, the unique characteristics of CP-Ti have a significant impact on the evolution and application of near- α Ti alloys. It combines strength, corrosion resistance, biocompatibility, and ease of manufacturing. These qualities enable the creation of high-performance materials tailored for diverse industrial applications.

Table 1. Composition of CP-Ti grades [37].

CP-Ti Grade	O content (max. wt.%)	Fe Content (max. wt.%)	σ 0.2 (Mpa)
Grade 1	0.18	0.2	170
Grade 2	0.25	0.3	275
Grade 3	0.35	0.3	380
Grade 4	0.4	0.5	480

2 Sintering

2.1 Sintering process of near- α Ti alloy

Sintering is an essential process in the fabrication of near- α Ti alloys, in which powdered components are consolidated and fused through the application of heat and pressure. This method aims to transform separate particles of loose powder into a dense, solid mass that has improved mechanical properties and a uniform microstructure. Sintering involves compressing Ti powder and alloying reinforcements into a green compact or preform, which is then subjected to temperatures below the melting points of the constituent components. As the temperature increases, diffusion mechanisms are activated, enabling atoms to migrate and establish chemical interactions at the interfaces between particles. Simultaneously, the application of pressure facilitates the reorganization and compaction of particles, resulting in the elimination of pores and the formation of a more dense structure. Sintering serves several essential purposes. Firstly, it enhances densification by reducing or removing voids, gaps, and other flaws within the material, hence enhancing mechanical strength, and toughness [26, 38, 39]. Furthermore, it offers the capacity to control the growth of grains within the material, hence modifying the microstructural characteristics and mechanical properties [40, 41]. The microstructure and mechanical properties can be enhanced by adjusting sintering parameters, such as temperature, duration, and pressure, in order to regulate the dispersion of grain sizes. Furthermore, sintering promotes the even distribution of the alloying elements inside the CP-Ti matrix, hence allowing the formation of essential phases and intermetallic compounds that are crucial for the alloy's properties [42]. Aluminium, vanadium, and zirconium have the ability to form solid solution-strengthening phases when combined with Ti. These phases enhance the mechanical properties and stability of the microstructure. The categories of sintering processes are shown in **Fig. 2**.

The process of sintering is crucial in determining the characteristics of near- α Ti alloys. Factors like temperature, time, pressure, and environment have a substantial influence on the microstructural evolution and mechanical properties of the developed product. The temperature at which sintering occurs affects the bonding between particles and the speed at which solid-state diffusion takes place [43]. The ideal sintering temperature range is typically 60% to 80% of the material's melting point [44], which corresponds to approximately 1006°C to 1342°C for near- α titanium alloys. Achieving the presence of β -Ti within the matrix requires the sintering temperature to exceed the beta-transus temperature, which varies depending on the alloying elements. For CP-Ti, the beta-transus temperature is 885°C [45]. While the specified temperature range is appropriate, researchers have reported that the optimum sintering temperature for near- α Ti alloys generally falls between 1000°C and 1200°C [24, 32, 46]. Elevated temperatures enhance particle mobility and densification; however, excessive temperatures can induce microstructural coarsening, leading to a degradation of mechanical properties. The duration of sintering impacts the consolidation

and diffusion of particles. Longer sintering times often lead to more denser microstructures, but they may also lead to grain growth. Applying pressure facilitates particle rearrangement and compaction, enhancing mechanical properties. However, excessive pressure can introduce defects such as microcracks, delamination, or residual stresses, which may compromise the integrity and performance of the material. By controlling the sintering environment through the use of inert gases or vacuum, oxidation is minimized, and desirable chemical reactions are facilitated. This allows for the creation of customized microstructures and enhanced alloy properties. Precise sintering conditions can be utilized to optimize near- α Ti alloys for specific applications, thereby improving properties like strength, toughness, and resistance to corrosion that are essential for high-performance industries.

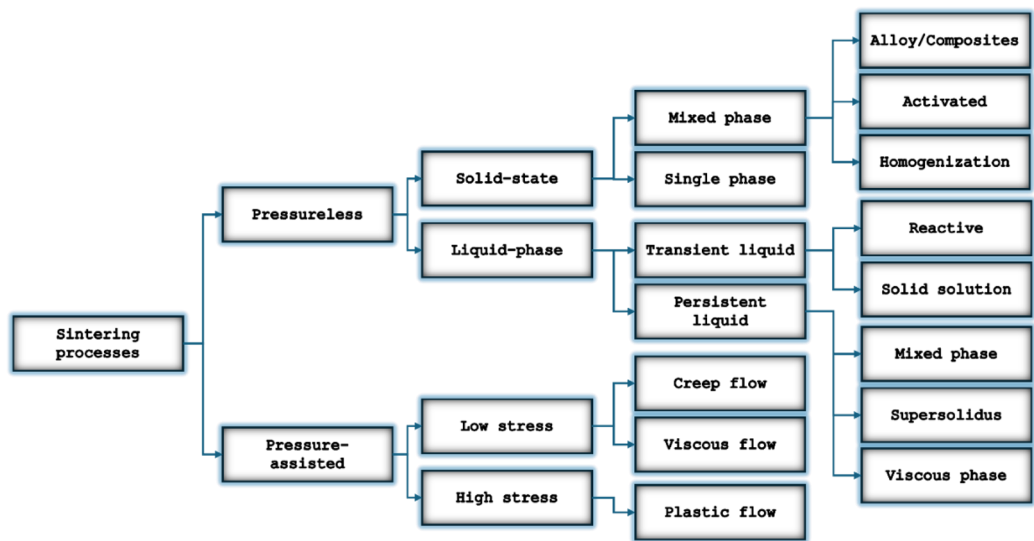


Fig. 2. The sintering process categories [47].

2.2 Experimental procedure for sintering

The sintering of near- α Ti alloys involves several essential phases that are necessary to attain the intended microstructure and characteristics. The experimental procedure of Ti alloys begins with powder preparation, a critical initial step. Here, CP-Ti powder and alloying element powders are carefully selected and blended to achieve the desired composition. The powders undergo modification in terms of particle size distribution and shape to facilitate uniform compaction during subsequent processes. Particle size distribution and shape in near- α titanium alloy powders are controlled through techniques such as ball milling, which refines particle size and ensures uniformity, and atomization methods like gas or plasma atomization, which produce spherical particles with improved flowability. Sieving is employed to separate particles into desired size ranges, while mechanical grinding or spray drying helps modify particle shapes for better packing density and compaction. These methods are essential for optimizing sintering behavior, ensuring uniform densification, and achieving desirable microstructural and mechanical properties in the final alloy. Following powder preparation, the blended powders are compacted into a green compact or preform

using methods like cold or hot pressing. This compaction stage requires precise pressure control to ensure adequate particle adherence and consolidation. The green compact forms the primary shape for the sintered object and must possess sufficient green strength to endure subsequent handling and processing phases. During this sintering process, solid-state diffusion occurs, leading to particle bonding and density increase. Precise control over temperature, time, and atmosphere is crucial to achieve desired modifications in microstructure and enhance material characteristics.

After sintering, the component is gradually cooled to ambient temperature to prevent thermal shock and minimize residual stresses [48]. Controlled cooling rates are employed to maintain microstructural stability and ensure the dimensional integrity of the fabricated sample [49, 50]. Post-sintering processing encompasses additional steps tailored to meet specific application requirements. These may include heat treatment, machining, surface finishing, or coating deposition, aimed at improving microstructure and properties to meet performance criteria. Quality control measures are implemented throughout the sintering and post-processing stages to verify product integrity and homogeneity. Non-destructive and destructive testing methods are used to evaluate mechanical, physical, and chemical properties, ensuring suitability for intended applications. Researchers can customize the evolved microstructure, mechanical properties, and performance of Ti alloys for diverse industrial uses, like aerospace components including medical implants, by meticulously controlling each aspect of the sintering process. This process ensures that the final product meets stringent performance and quality standards. **Fig. 3.** shows the representative chart for the sintering procedures. Stages I, II, and III depict particle rearrangement (compacting the powder to achieve optimal packing through applied pressure), solution precipitation (the rise in temperature creates a partial liquid phase, facilitating rapid particle movement, which leads to neck formation between particles and reduced porosity until the end of the sintering holding time), and final densification (rapid decrease in temperature, resulting in thermal contraction of the samples), respectively.

3 Near- α Ti alloy development

Near- α Ti alloys' properties are primarily influenced by their processing techniques, heat treatment methods, chemical composition, and microstructure. Alloying elements are commonly added to Ti alloys to control their constituents, modify phase transformation kinetics, and enhance solid-solution strengthening within the microstructure [51]. The alloying elements are classified as neutral, α -stabilizers, or β -stabilizers depending on their influence on the β -transus temperature. β -stabilizers like V, Mo, Ta, and Nb decrease the β -transus temperature, whereas α -stabilizers such as Al, O, C, and N increase it. Neutral elements like Zr and Sn have minimal impact on the β -transus temperature but strengthen the α -phase. The presence of Al and other interstitial elements has a tendency to increase the stability of the α -phase, resulting in an elevation of the temperature at which the β -phase transformation occurs. Most alloying additions stabilize the β -phase by reducing the transformation temperature, particularly those that act as beta stabilizers. Elements like Sn and Zr are neutral, reinforcing the α -phase without affecting the transformation temperature significantly. **Fig. 4.** explains the different types of alloying elements and their effects on the β -transus temperature.

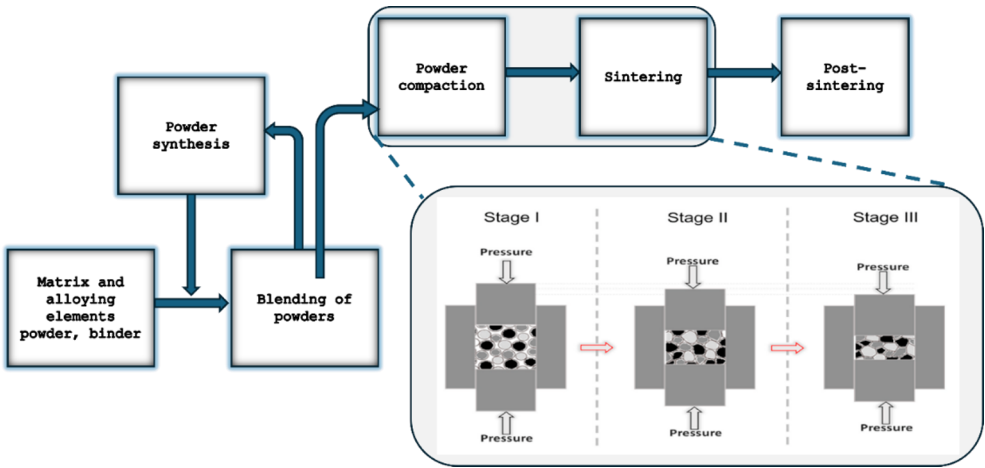


Fig. 3. Sintering procedures chart (adapted from [32] and [52]).

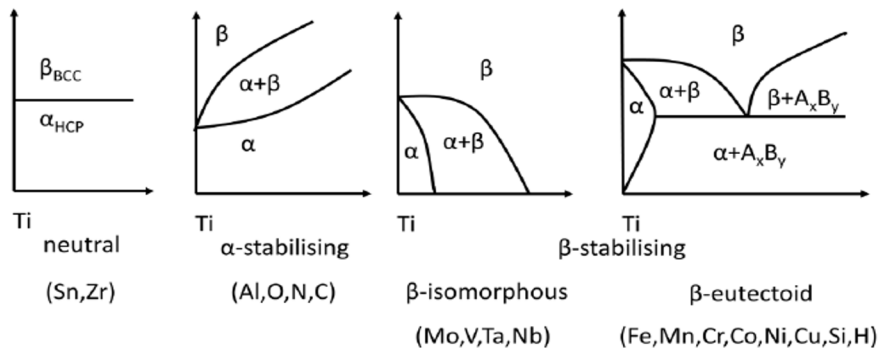


Fig. 4. Ti phase diagram showing the effect of alloying elements [53].

Near- α Ti alloys typically contain approximately 1–2 wt% of β -stabilizing element(s), which can stabilize around 5–10% of β -phase within the alloy's structure at room temperature [3]. The incorporation of a small percentage of the β -phase within the predominantly α -phase matrix, achieved through controlled amounts of β -stabilizing elements, facilitates dual-phase strengthening by effectively managing the morphology and distribution of the phases within the alloy. The development of near- α Ti alloys focuses on optimizing alloy composition, microstructure, and processing techniques to achieve an optimal blend of superior strength, good formability, and excellent toughness. Heat treatment processes are also utilized to tailor the microstructure and mechanical properties, with solution treatment, then controlled cooling and aging for grain structure refinement and properties optimization [54]. Various processing techniques like hot working and cold working are employed to further enhance microstructure and mechanical strength. Considerations for corrosion resistance and application-specific requirements drive the development of near- α Ti alloys, ensuring they meet the demanding performance criteria of industries such as aerospace and biomedical sectors. **Fig. 5.** illustrates the optimization of various factors, including composition, preparation techniques, and post-heat treatments, which are crucial for developing near- α

titanium alloys with enhanced strength and ductility through a bimodal or multimodal structure.

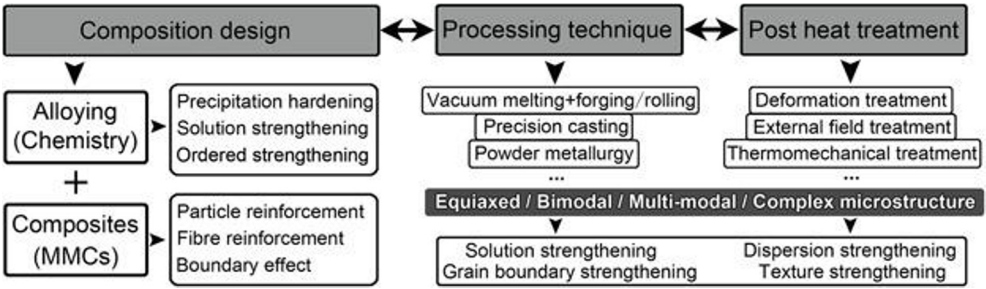


Fig. 5. Strategies for the fabrication of near- α Ti alloy/composites [51].

3.1 Alloying elements

Alloying in the near- α Ti commonly involves the development of an alloying system of Ti-Al-Sn-Zr-V-Nb-Mo-Si where Nb, Mo, and Si are the β -stabilizers not more than 2 wt.% as noted by Babu et al. [55]. Researchers have explored substituting expensive strong β -stabilizing elements like V, Nb, and Mo with more cost-effective β -eutectic options like Fe, Mn, and Cr [56, 57]. Nevertheless, Fe can negatively impact ductility in near- α Ti alloys because of intermetallic phase formation [58]. According to Jawed et al. [56], the trade-off observed in strength-ductility can be mitigated by employing Si. Alloying elements typically dissolve in both the body-centered cubic (bcc) β -phase structure at high-temperature and hexagonal close-packed (hcp) α -phase structure at low-temperature, resulting in alloys with refined microstructures based on the type of element(s) utilized for alloying and the cooling type after sintering [59, 60].

Aluminium (Al) serves as the principal α -stabilizing element in Ti alloys, offering key benefits such as solid solution hardening due to its solubility in both α and β -phases [61]. It is readily available, cost-effective, and has a lower density compared to other elements used in alloying. Al is extensively utilized in near- α Ti alloys to enhance creep resistance and tensile strength while maintaining low density. The addition of Al, up to certain limits, results in the precipitation of a creep-resistant and thermally stable aluminide phase within the Ti matrix. However, exceeding certain Al content levels can lead to brittle Ti aluminide intermetallic compound formation, limiting the amount of Al that can be effectively added to optimize alloy properties. In commercial alloys, Al performs a critical role in the strengthening of the α -phase at both ambient and elevated temperatures, making it a vital component in near- α Ti alloys. The work of Huang et al. [62] focused on investigating the strengthening effects of Al in Ti-6Al alloy and CP-Ti, highlighting how the addition of Al significantly increased the UTS of Ti-6Al to 684 MPa compared to 260 MPa for pure Ti, albeit with reduced ductility and impact toughness. They attributed this strength enhancement to Al atoms dissolution, altering the configurations of the atomic bond and electronic structures within the α -Ti lattice, which improved dislocation nucleation resistance, deformation twinning, and gliding. Despite the strength gains, Al's inhibitory effect on deformation twinning and dislocation activities resulted in decreased impact toughness and plasticity. Jeje et al. [3] compared microhardness and wear results of CP-Ti and Ti-xAl-1Mo with Al wt.% variations from 3-7 fabricated by spark plasma sintering (SPS) as seen in Fig.6., revealing significantly higher microhardness and wear resistance in Ti-xAl-1Mo alloys as Al

weight fraction increased from 3 to 7 percent. This enhancement was attributed to Al's solid solution strengthening ability and its promotion of direct interaction between solute atoms and dislocation cores, leading to increased dislocation density per unit strain with higher Al content. These findings collectively emphasize how Al reinforcement in near- α Ti alloys can enhance the strength at the cost of reduced ductility, providing critical insights for optimizing alloy design. However, in the fabrication of near- α Ti alloys, the weight percentage (wt.%) of Al should be kept below 10 to inhibit ordering or α_2 precipitation within the α -phase [63].

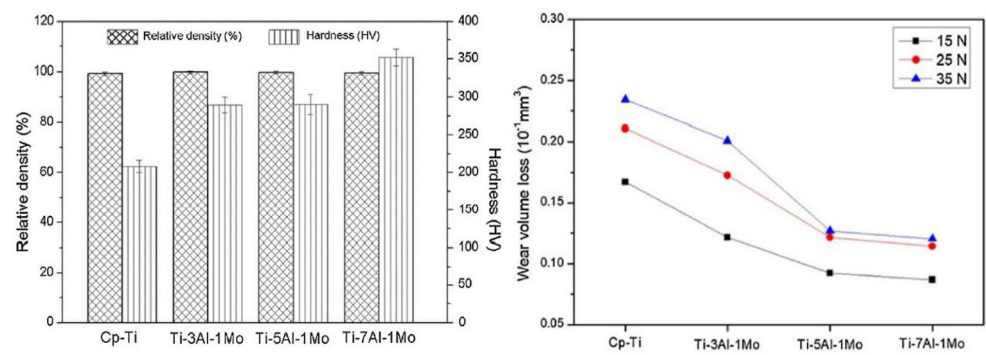


Fig. 6. Comparison between microhardness and wear volume loss of CP-Ti and Ti-xAl-1Mo near- α Ti [3].

Molybdenum is a biocompatible β -stabilizer that enhances the properties of near- α Ti-alloy by increasing its strength, toughness, and corrosion resistance [32, 64]. Furthermore, it improves the alloy's ability to resist wear and retain its dimensional stability. Molybdenum forms carbide and nitride particles inside the alloy structure, which enhance the processes of strengthening and impede the development of grains while the sintering process is on [65, 66]. The studies of Kumar et al. [67], Rajadurai et al. [68], and Xu et al. [69], investigations focused on the effects of molybdenum (Mo) additions on Ti-based alloys fabricated via different sintering techniques and their subsequent characterization. Kumar et al. [67] utilized SPS at 1200 °C to produce Ti-based alloys with Mo concentrations with 4 to 20 wt% variation. They observed that increasing Mo content altered microstructural evolution and densification behavior, reaching a peak relative density of 99.9% at 16 wt% Mo [60]. Conversely, Rajadurai et al. [68] explored pre-alloyed Ti6Al4V-xMo alloys with 0-6 wt.% of Mo using SPS, demonstrating a shift in microstructure from equiaxed α -phase and Widmanstätten ($\alpha + \beta$ phase) to a duplex and globular structure as the Mo content increases. Mo acted as a solid solution-strengthening agent, enhancing the yield strength and UTS, albeit with reduced ductility. Fractography analysis revealed a transition to brittle fracture behavior with higher Mo content. Additionally, Xu et al. [69] investigated microwave-sintered porous Ti-Mo alloys, highlighting the impact of Mo content on phase composition, pore structure, and mechanical properties. The β -phase volume fraction increased with higher Mo content, leading to larger pore sizes and reduced mechanical strength. However, these porous alloys' resistance to corrosion was not substantially impacted by the Mo concentration., demonstrating excellent cytocompatibility with cell viabilities exceeding 94%. Depending on the Mo concentration, the Ti-alloys' microstructure is composed of α , $\alpha + \beta$, $\alpha + \beta + \omega$, or β -phase [67]. However, in the fabrication of near- α Ti-alloy the wt.% of Mo should be between 1-2 [4].

Vanadium (V) is widely utilized for near- α Ti alloy fabrication because of its ability to enhance mechanical properties, refine grain size, and act as a β -phase stabilizer [70, 71]. It forms solid solution-strengthening phases with Ti, leading to increased hardness and strength

of the alloy, while also augmenting the formation of β -phase precipitates that reinforce the alloy matrix [71]. An et al. [71] explored the influence of the content of V on the microstructural evolution and strength of 2 and 4 wt.% addition of V to Ti-6Al alloys fabricated employing Wire + Arc Additive Manufacturing (WAAM) technology. Distinct microstructural features were observed (**Fig. 7.**), with irregular α grains, and plate-like structures in Ti-6Al alloy, while the Ti-6Al-2V alloy exhibited columnar grains with an enlarged β grain size due to the 4% V addition. Different V contents led to lamellae α and acicular α' structures for 2 and 4 wt.% V reinforced samples, respectively. The Ti-6Al-2V alloy exhibited a combination of lamellar α -phase and retained β -phase laths within larger β grains (**Fig. 7d**). Conversely, the Ti-6Al-4V alloy was predominantly characterized by an acicular α' network structure (**Fig. 7e**). Increasing V content led to a consistent increase in yield strength and UTS but decreases in impact toughness and fracture strain. Lower V content led to enhanced impact toughness, elongation, and reduced strength, attributed to solid solution strengthening and lamellar toughening effects from V. Notably, Ti-6Al alloy exhibited significantly higher impact toughness (47.4% increase) in comparison to Ti-6Al-4V, emphasizing the critical role of alloy composition in determining mechanical properties. Similarly, Sherif et al. [72] evaluated the impact of V content on the corrosion behavior of Ti6AlxV ($x = 2, 4, 6$, and 8 wt%) alloys exposed to 3.5% NaCl solutions. Produced via mechanical alloying followed by sintering, the alloys demonstrated enhanced corrosion resistance with increasing V content, attributed to oxide film formation on alloy surfaces, more pronounced with longer immersion times (from 1 to 48 hours). Electrochemical measurements showed reduced corrosion rates (j_{Corr}) and resistances (R_{Corr}) with higher V content, minimizing uniform corrosion and preventing pitting, confirmed by SEM and EDX analyses. The study emphasizes V's role in the enhancement of Ti-alloys' corrosion resistance. Just like Molybdenum, vanadium is commonly used as β -stabilizers in near- α Ti alloys due to their effective β stabilization properties, cost-effectiveness as master alloys, and minimal solidification segregation tendencies. According to Fu et al. [28] V enhances the fatigue and thermomechanical working performance of Ti (Ti) alloys under high-temperature, high-cycle conditions. However, in developing near- α Ti-alloy, the wt.% of V should be between 1-4 %.

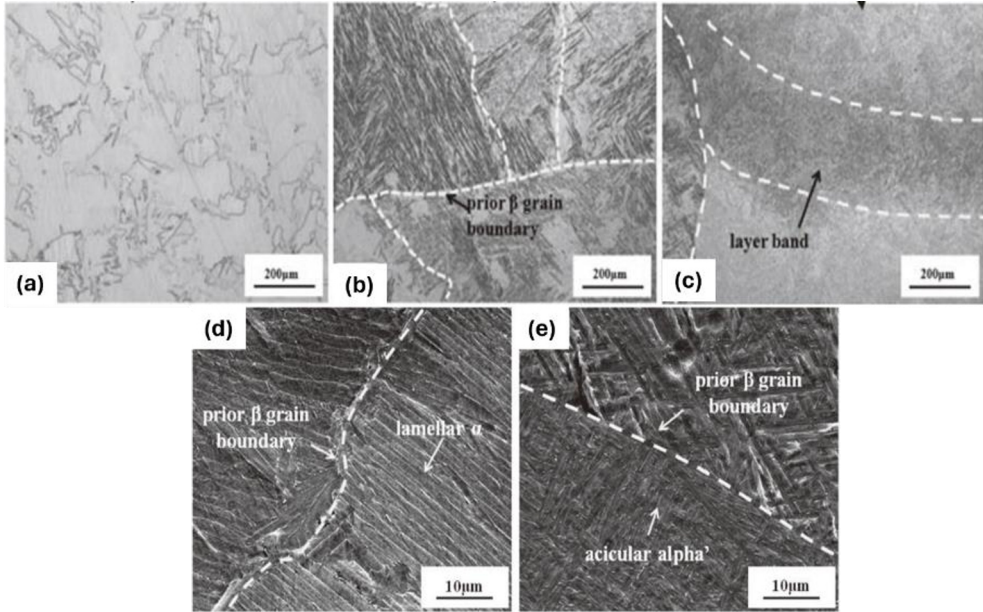


Fig. 7. SEM images for (a) Ti-6Al (b and d) Ti-6Al-2V (c and e) Ti-6Al-4V [71].

Niobium (Nb) is non-toxic and often utilized as a β -phase stabilizer in near- α Ti alloys. Its role is to promote the creation of small β -phase precipitates, which in turn improve the alloy's strength, toughness, and corrosion resistance [73, 74]. Niobium also enhances the process of microstructural refinement and regulates the level of microstructural coarsening during sintering, leading to enhanced mechanical characteristics and dimensional stability. After conducting an extensive literature search, to the best of our knowledge, there were few reported variations involving niobium (Nb) in the development of near- α Ti alloys, despite the existence of numerous near- α Ti alloys containing approximately 0.7 wt.% of Nb. However, the results of our investigation into the effects of Nb variation on Ti-alloys are discussed below, providing valuable insights into Nb as an alloying element. The studies by Han et al. [75], Zhang et al. [76], and Fikeni et al. [74] collectively emphasize the significant impact of Nb as an alloying element in the development of Ti-based alloys for biomedical applications. Han et al. [75] investigated Nb variation in Ti-Nb alloys from 5 to 20 wt%, revealing that increase in Nb content led to a higher volume percentage of the ω -phase and improved mechanical properties, resistance to corrosion, and biocompatibility, highlighting the potential benefits of Nb alloying. Zhang et al. [76] explored the effect of 0–25 wt.% Nb content on CP-Ti, showing that these alloys exhibited enhanced mechanical properties, including increased hardness, ultimate strength, and yield strength compared to CP-Ti, along with improved corrosion resistance and biocompatibility. Ti-Nb alloys were identified as good prospects for biomedical implants. Fikeni et al. [74] focused on how the microstructure Ti-Nb alloys evolves and the study of the mechanical properties based on 13 and 28 wt.% variation of Nb content. An evolution from a martensitic structure to a stabilized β -phase was observed with increasing Nb content, resulting in decreased Young's modulus but increased micro-hardness. Yamabe-Mitarai et al. [77] found that the oxidation enhancement effect of adding Nb was more pronounced in Ti-8.7Al compared to Ti-5.8Al. Interestingly, the impact of adding approximately 9 wt.% Nb was equivalent to adding 4 wt.% Nb, suggesting that the enhancement of oxidation resistance reaches a saturation point with a 4 wt.% Nb addition for

Ti-Al alloys. However, in the development of near- α Ti-alloy, the wt.% of Nb should be between 1-3.

In near- α Ti alloy development, the effect of tin (Sn) and zirconium (Zr) as alloying elements is significant. They (Sn and Zr) both exhibit the characteristics of a neutral alloying element [78]. They contribute to solid solution strengthening and grain refinement without strong phase stabilization effects primarily enhancing the microstructural characteristics and mechanical properties [78, 79]. They have a vital role in strengthening the α -phase, which is essential for maintaining desired mechanical properties and resistance to corrosion. Overall, both Sn and Zr contribute positively to the performance of near- α Ti alloys, with Sn enhancing mechanical properties and Zr primarily influencing phase stability and corrosion resistance. Dal Bó et al. fabricated and characterized low-cost Ti-Nb-Fe-based quaternary alloys incorporating Zr and Sn to enhance mechanical properties for structural biomaterials. Tensile testing of aged Ti-19Nb-2.5Fe-6Sn revealed a remarkable 1271 MPa yield strength and 90 GPa elastic modulus close, achieving about 1.5 elastic admissible strength (EAS). Ti-19Nb-2.5Fe-10Zr alloy that was solution-treated exhibited a favorable blend of yield strength (1027 MPa) and elastic modulus (69 GPa). The study highlighted the role of Sn in enhancing yield strength and refining the secondary α -phase, while Zr primarily reduced the elastic modulus. Zirconium readily forms intermetallic compounds with Ti, such as (Zr, Ti) [80], that can serve as nucleation sites for α -phase precipitation. By suppressing the formation of ω (omega) phase, Zr and Sn contributed to low-modulus, cost-effective quaternary alloys suitable for orthopedic implants. However, in developing near- α Ti-alloy the wt.% of Zr should not exceed 5 as it can reduce the solubility of some other alloying elements like Si [81].

Studies have shown that the addition of small Si wt.% in near- α Ti alloys improves their mechanical properties, majorly the ability to resist deformation under constant stress (creep resistance) [82]. On the other hand, the existence of sizable silicide particles can have an adverse effect on the alloy's fatigue properties and ductility [81]. To avoid the formation of silicide precipitation and related problems, it is crucial to keep the silicon concentration below the maximum solubility of 0.2 wt% in pure Ti at 600 °C [81]. In the study of Yamabe-Mitarai et al. where 0.5 wt.% of Si was introduced to Ti-10Al-2Nb-2Zr, it was observed that there was a deterioration in the oxidation resistance of the near- α Ti-alloy despite the enhancement in creep. Most of the developed near- α Ti employs below 0.5 wt.% of Si [83-86].

The selection and balancing of these typical additives in near- α Ti alloys are done meticulously to achieve the required combination of attributes. Each additive serves specific functions in enhancing the overall performance of the material. Engineers can customize the microstructure and characteristics of near- α Ti alloys to suit specific application needs, such as aerospace parts or medical implants, by optimizing the composition and concentration of additives. Table 2 shows the range of some alloying elements employed in near- α Ti development and the corresponding effects on Ti-alloy's microstructure and properties. However, the range cited in this study can be further varied based on the wt.% of other alloying elements and the specific applications for which the developed alloy is intended.

Table 2. Alloying elements and the effects on CP-Ti properties

Alloying Element	Range (%)	Effect on Microstructure and properties	Effect on Mechanical Properties	Effect on Oxidative/Corrosion Properties
Aluminum (Al) [62, 87, 88]	2-10	Refines grain structure, stabilizes α -phase, reduces density	Increases strength and toughness	Improves corrosion resistance, particularly in oxidizing environments
Zirconium (Zr) [81]	1-5	Controls grain growth, refines microstructure	Enhances strength and creep resistance	Improves resistance to corrosion and oxidation
Tin (Sn)	1-3	Stabilizes β phase, refines grain size	Increases tensile strength	Enhances resistance to corrosion, especially in acidic environments
Vanadium (V) [70, 71]	1-4	Forms fine precipitates, strengthens grain boundaries	Improves strength and fatigue resistance	Enhances resistance to oxidation at elevated temperatures
Molybdenum (Mo) [4, 66, 68]	1-5	Forms stable carbides/nitrides, refines microstructure	Increases strength, hardness, and toughness	Enhances resistance to pitting and crevice corrosion
Niobium (Nb) [75-77]	1-3	Stabilizes β phase, controls grain growth	Improves strength and ductility	Enhances resistance to intergranular corrosion and oxidation
Silicon (Si) [78, 81]	0.05-0.5	Suppresses β -phase formation, refines microstructure	Enhances strength and creep resistance	Improves resistance to oxidation and high-temperature corrosion

4 Challenges and future directions

Sintering near- α Ti alloys presents significant challenges that must be overcome to achieve optimal alloy performance and manufacturing efficiency. One key challenge is achieving uniform densification without introducing unwanted phases or defects during sintering, particularly due to the high oxygen affinity of these alloys, which can lead to oxygen pickup and impact mechanical properties [89]. Another hurdle involves selecting appropriate sintering additives that not only promote densification but also enhance microstructural and mechanical properties while ensuring compatibility with Ti and maintaining alloy stability. Controlling grain size and microstructure during sintering is crucial for achieving desired mechanical properties like strength and ductility, necessitating careful balancing of sintering conditions including temperature, pressure, and atmosphere to achieve the desired microstructure without compromising alloy integrity [51]. Moreover, scalability and cost-effectiveness in industrial applications pose challenges, requiring optimization of production parameters to reduce processing time and energy consumption while upholding quality standards. Addressing these obstacles demands interdisciplinary research efforts spanning material science, metallurgy, and process engineering to fully leverage the potential of near- α Ti alloys for high-performance applications in aerospace, automotive, and medical industries.

Advancements in sintering technology are reshaping the trajectory of near- α Ti alloys, introducing innovative strategies to tackle existing hurdles and opening up new avenues for alloy enhancement. Several emerging trends are propelling progress in sintering methodologies. Firstly, advanced Additive Manufacturing (AM) techniques like selective laser melting (SLM) and electron beam melting (EBM) are revolutionizing Ti alloy production by enabling precise control over microstructure and composition, facilitating the creation of intricate components with customized properties. Secondly, in-situ alloying and synthesis methods are gaining traction, allowing for the direct introduction of alloying elements during sintering to enhance properties and mitigate traditional powder metallurgy challenges. Thirdly, the utilization of nanostructured materials as sintering additives shows promise in improving densification and controlling grain growth due to enhanced reactivity and diffusion kinetics. Moreover, the integration of computational modeling and simulation tools is optimizing sintering parameters and predicting material behavior, expediting alloy design and process development while reducing experimental iterations. Techniques such as phase field modeling, thermodynamic modeling (e.g., CALPHAD), finite element analysis, molecular dynamics simulations, and process simulation software help predict microstructural evolution and mechanical behavior. Additionally, machine learning approaches analyze large datasets to accelerate the design process, ultimately leading to advanced materials with tailored properties. Additionally, the development of environmentally friendly "green" sintering technologies such as SPS and microwave sintering offers energy-efficient alternatives with shorter processing times and lower environmental impact. Lastly, automation and integrated process control systems enable real-time monitoring and adjustment of sintering conditions, ensuring consistent quality and repeatability crucial for large-scale applications. These emerging trends underscore the dynamic evolution of sintering technology in near- α Ti alloy development, providing a pathway for addressing current challenges and advancing the next generation of high-performance Ti alloys tailored to specific application needs.

To propel the field of near- α Ti alloy sintering and fully harness their capabilities across diverse industries, several critical areas require focused research and development efforts. Firstly, optimizing sintering parameters—including temperature, pressure, and atmosphere—is essential to understand their impact on alloy microstructure and mechanical properties, facilitating optimal densification and performance through advanced modeling techniques. Secondly, exploring innovative sintering additives and assessing their compatibility with CP-Ti are crucial for enhancing alloy stability and properties, necessitating rigorous evaluation of additive-Ti interactions. Thirdly, developing strategies for precise microstructural control and grain refinement during sintering is key to tailoring mechanical properties like strength, ductility, and fatigue resistance. Furthermore, investigating tailored alloy designs with specific compositions and microstructures optimized for aerospace or biomedical applications using computational tools is imperative. For instance, the development of multifunctional near- α Ti alloys as functionally graded materials (FGMs) using advanced sintering techniques (e.g. SPS) holds significant potential. These gradient structures can optimize mechanical and thermal properties by varying composition and microstructure throughout the material, making them ideal for high-performance applications in aerospace and biomedical fields. Future studies should focus on the fabrication of near-alpha titanium/hydroxyapatite FGMs to enhance biocompatibility and mechanical strength for biomedical implants, as well as exploring gradient porous designs that mimic the mechanical properties of human bone for effective bone replacement applications. This approach could pave the way for tailored materials that meet specific performance requirements in critical applications. Advanced characterization techniques such as electron microscopy and X-ray

diffraction are indispensable for assessing microstructural evolution and mechanical behavior, providing insights into performance correlations. Addressing scalability and cost-effectiveness challenges in sintering processes while prioritizing quality and consistency for industrial-scale manufacturing is critical. Embracing green sintering technologies to reduce environmental impact and energy consumption, alongside exploring multifunctional alloys with integrated properties like corrosion resistance and biocompatibility, holds immense potential. By focusing on these areas of research and development, the scientific community can advance the understanding and application of near- α Ti alloys, driving innovation in high-performance materials for diverse industrial sectors.

5 Conclusion

In conclusion, our investigation into sintering additives alongside CP-Ti for near- α Ti alloys has provided valuable insights into alloy processing and development. Sintering additives play a crucial role in promoting densification and shaping microstructural evolution during alloy fabrication while understanding their compatibility and interactions with titanium is fundamental for optimizing alloy properties. Furthermore, advanced sintering techniques like additive manufacturing and in-situ alloying offer innovative ways to customize microstructure and composition, paving the way for exciting possibilities in alloy design. To enhance sustainability, it is vital to explore environmentally friendly sintering approaches such as hydrogen sintering, the use of biomass-derived reductants, low-temperature sintering, and incorporating recycled powders, as these methods can significantly reduce carbon emissions, enhance resource efficiency, and lower energy consumption. Despite these advancements, challenges remain regarding the scalability and cost-effectiveness of sintering technologies such as high equipment and material costs, variability in process optimization, energy consumption, difficulties in scaling innovative techniques, and the need for consistent quality control; addressing these issues requires a multi-faceted approach that includes developing modular systems, researching cost-effective materials, utilizing computational modeling for process optimization, implementing energy-efficient techniques, conducting pilot studies for scaling, and establishing standard quality protocols to enhance reliability and facilitate industrial adoption. Future research should focus on optimizing sintering processes and exploring new additive materials that can enhance alloy performance and stability, including the development of novel sintering additives and the application of computational modeling for process optimization. Additionally, investigating multifunctional alloy designs that meet specific performance requirements, alongside the exploration of environmentally friendly sintering techniques and their scalability, will be critical for advancing sustainable materials development. By fostering interdisciplinary collaboration and pursuing practical solutions, we can address current challenges and unlock the full potential of near- α Ti alloys across various critical applications.

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