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# Chapter

# Processing of Beta Titanium Alloys for Aerospace and Biomedical Applications

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#### **Abstract**

The unique combination of attributes—high strength to weight ratio, excellent heat treatability, a high degree of hardenability, and a remarkable hot and cold workability—has made beta titanium alloys an attractive group of materials for several aerospace applications. Titanium alloys, in general, possess a high degree of resistance to biofluid environments; beta titanium alloys with high molybdenum equivalent have low elastic modulus coming close to that of human bone, making them particularly attractive for biomedical applications. Bulk processing of the alloys for aerospace applications is carried out by double vacuum melting followed by hot working. There have been many studies with reference to super-solvus and sub-solvus forging of beta titanium alloys. For alloys with low to medium level of molybdenum equivalent, sub-solvus forging was demonstrated to result in a superior combination of mechanical properties. A number of studies have been carried out in the area of heat treatment of beta titanium alloys. Studies have also been devoted to surface modification of beta titanium alloys. The chapter attempts to review these studies, with emphasis on aerospace and biomedical applications.

**Keywords:** beta titanium alloys, titanium melting, thermomechanical processing, surface modification, aerospace and biomedical applications

#### 1. Introduction

Titanium was discovered in 1791, but it came into effective application only in the 1950s. After 115 years, i.e., in the year 1906, M. A Hunter at General Electric Company prepared pure titanium for the first time [1]. Since 1950s, titanium holds a prime position in aerospace, biomedical, automotive, and chemical processing industries due to unique features listed below:

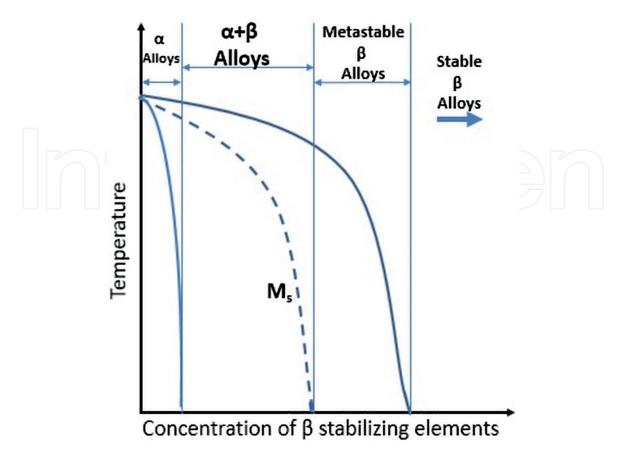
- 1. Low density (60% of steel or super alloy's density),
- 2. Higher tensile strength (Higher than ferritic stainless steel and comparable to martensitic stainless steel and Fe- base superalloys)
- 3. Higher operating temperature (Up to 595°C for commercially available alloys and >595°C for titanium aluminides)

- 4. Excellent corrosion resistance (Higher than stainless steel and biocompatible)
- 5. Forgeability
- 6. Castability (Mostly by investment casting)

Despite being the fourth-most abundant structural metal available in the earth crust, its commercial exploitation has been low compared to steel and aluminium due to high cost of production.

Pure Titanium has an hcp crystal structure. Due to the allotropic nature of titanium, the room temperature hcp crystal structure (alpha phase) will be transformed to bcc (beta phase) structure on heating to a particular temperature called beta transus temperature (882.5°C). Alloying elements of titanium are classified on the basis of their influence on the transus temperature. For example, if the transus temperature is increased on the addition of the certain elements, then they are called as alpha stabilisers (Al, O, N, and C); similarly there are some other elements which bring the transus temperature down and they are termed as beta stabilisers (V, Mo, Ta and Nb). The elements Sn and Zr have little or no effect on transus temperature and are termed as neutral elements.

Beta alloys form the metastable beta phase upon quenching rather than undergoing martensitic transformation. A schematic representation of the beta isomorphous phase diagram is shown in the **Figure 1**. Beta alloys can also be classified as those which have alloy which has enough beta stabilisers to avoid the martensitic start ( $M_s$ ) pass through upon quenching. Beta alloys are further classified into metastable and stable beta alloys based on the content of beta stabilisers. Commercially available beta alloys are metastable beta alloys and stable beta alloys are not commercially available [2]. The metastable beta phase can precipitate the fine alpha



**Figure 1.**Beta isomorphous phase diagram.

phase upon ageing/thermal treatment. Hence, beta alloys are hardenable and can attain a higher strength level than alpha + beta alloys and higher specific strength compared to many other alloys [3].

Corrosion resistance of beta alloys is also found to be better than that of alpha + beta alloys. Higher hydrogen tolerance makes beta alloys to perform better in the Hydrogen-rich environments [2]. Increased fracture toughness for a given strength level and amenability to room temperature forming and shaping are superior attributes compared to alpha + beta alloys [1]. Ti-13V-11Cr-3Al (B120VCA) was the first beta alloy produced/developed and used in the SR-71 (Surveillance aircraft) as a sheet product.

Beta alloys' inherent characteristics such as pronounced ductility owing to the crystal structure (bcc), heat treatability, and superior cold rollability make them an effective alternative to alpha + beta alloys [4]. Furthermore, beta alloys have lower beta transus temperature than the alpha + beta alloys [5]. Hence, beta alloys are considered to be the economical choice in perspective of processing compared to the alpha + beta alloys. For example, despite the higher formulation cost, Ti-15V-3Al-3Cr-3Sn alloy's thinner gauges (<2 mm thick) cost one-tenth of those of Ti-6Al-4V [3].

# 2. Processing of beta alloy

## 2.1 Melting

The initial step is the fabrication of ingot from sponge for conversion to mill products. The melting practices to produce beta titanium alloy ingots can be broadly categorised into Vaccum Arc Remelting (VAR) and Cold Hearth Melting.

The conventional method used for the melting of beta titanium alloys is the Vacuum Arc Remelting (VAR) in a consumable arc furnace. In VAR, the furnace is initially evacuated for required vacuum and a dc arc is struck between the two electrodes. Here a consumable electrode (material to be melted) is employed as the cathode and starting materials such as titanium-based metal chips or machine turnings act as the anode. The consumable electrode can be fabricated from either of the two strategies.

- From the compacted sponge and/or scrap
- From plasma/electron beam hearth melting

Among these methods, the first method of predensification by compacting using a hydraulic press is widely used to fabricate electrodes. Compacted electrodes with nominal alloy composition are made by the pressing of blended clean and uniform-sized titanium sponge and alloying elements devoid of any harmful inclusions. These compacts (called as briquettes) are then assembled with bulk scrap to form the first melt electrode (called as a stick) by appropriate welding methods.

Finally, these fabricated electrodes are placed inside a vacuum furnace. When the electric arc is established, associated heat generation will result in the dripping of molten metal down to the water-cooled copper crucible to form the ingot. Initially, a layer of solid titanium or skull will be formed on the surface of cooled copper crucible which will hold the subsequently falling molten metal. In order to ensure chemical homogeneity, the ingots will be inverted and remelting will be performed. Ingots produced during first stage melting are again used as consumable electrodes during double or triple remelting. In addition to this, electrical coils are

provided in most of the VAR furnaces to generate an electromagnetic field capable of stirring the molten metal thereby further enhancing the homogeneity. Cold hearth melting is another developing technique which uses either plasma arc (PAM) or electron beam (EBM) melting furnace.

Proper monitoring should be ensured to control the solidification of beta titanium based ingots. Specifically, beta eutectoid compositions containing Fe, Mn, Cr, Ni and Cu are associated with depressed freezing temperatures [2]. This allows for solidification over a significant temperature range, consequently leading to solute segregation during solidification of the ingot. Such type of segregation results in regions with lower beta transus and results in a microstructure distinctive from the surrounding material. These solute segregated regions are clearly visible in beta titanium alloys subjected to heat treatment below/near to beta transus and are termed as beta flecks. Beta flecks, which range from a scale of few hundred micrometres to a few millimetres, can act as crack nucleation sites leading to fatigue failure. Beta flecks are mostly developed in large diameter ingots. However, beta isomorphous alloys containing Nb, Mo and V are not associated with these depressed solidification temperatures and are less prone to solute segregation.

Lower values of tensile ductility and low cycle fatigue life of near- $\beta$  Ti alloy Ti–10V–2Fe–3Al was found to be due to the presence of beta flecks [6]. Under tensile loading, crack nucleation occurred at beta fleck grain boundaries leading to intergranular and quasi-cleavage fracture. In the case of fatigue loading, the inhomogeneous strains developed due to the presence of beta flecks accelerated the crack nucleation and early crack propagation.

#### 2.2 Casting

For an expensive material such as titanium, casting is the perfect choice in attaining a (near) net shape in the fabrication of components with complex geometry without incurring much wastage. A significant weight (35%) saving can be achieved by employing the titanium casting instead of stainless steel casting in B-777 aircraft [7]. In general, rammed graphite mould and investment casting were utilised in titanium casting. Investment casting is preferred to obtain thin sections and better surface finish [8]. Ti-5Al-5V-5Mo-3Cr castings followed by HIP (Hot Isostatic Pressing) possess a superior strength compared to hipped Ti-6Al-4V castings with almost same ductility [9]. To extend brake life of fighter aircraft (F-18 EF) Ti-15V-3Al-3Cr-3Sn castings were used instead of Ti-6Al-4V castings due to the higher specific strength of the former [10].

#### 2.3 Forging and rolling

#### 2.3.1 Ingot breakdown forging

To exploit the ductile nature of the beta phase (bcc crystal structure), even for alpha and alpha + beta alloys, ingot break down forging is done above the beta transus temperature. In general, to avoid thermal stress cracking, titanium alloys are subjected to preheating before high-temperature forging.

Forging is performed to produce billets and bars of titanium with the optimum combination of strength and ductility [11]. Forging is performed using hydraulic presses. Both straight-forging and upset forging are performed in case of Ti alloys. For greater deformation and larger size, upset-forging is preferred [1]. Higher reactivity of the titanium demands the inert / vacuum processing to prevent surface contamination during high-temperature processing [1]. Drawing operation of titanium is prone to galling and seizing. Hence, proper lubricants have to be employed

to avoid those effects [1]. Compared to all other Ti alloys, beta alloys can withstand high pressure before cracking. Ti- 13V-11Cr-3Al can withstand up to 690 MPa without cracking. In contrast, Ti-6Al-4V can withstand 585 MPa before cracking [1].

The microstructure of the ingots of beta alloys varies from small equiaxed grains (at the surface) to elongated columnar grains and large equiaxed grains at the bulk/centre of the ingot [4]. Beta Ti alloys are more suitable for low temperature working without being vulnerable to rupture or cracking compared to other Ti alloys [1] and this effect is attributed to the availability of enough slip systems to accommodate the deformations.

#### 2.3.2 Secondary forging

Secondary forging refers to the forging process employed to obtain the final shape/components. The temperature required for this kind of forging is lower than that for ingot breakdown forging. Unlike alpha and alpha + beta alloys, beta alloys show a significant increase in strength at high strain rates [1]. Hence, higher pressures are to be applied for forging of beta alloys; the pressure required to induce crack during forging is higher for beta alloys compared to alpha and alpha + beta alloys [1]. Beta titanium alloys have a broader range of forging temperature compared to alpha/alpha + beta alloys.

Due to the lower beta transus temperature, beta alloys have lower hot working temperature compared to alpha and alpha + beta alloys, For example, Ti–10V–2Fe–3Al has a secondary working temperature range between 700–870°C [12]. Types of forging and features are given in the **Table 1**.

#### 2.3.3 Rolling

Unlike other alloys, rolling of titanium requires higher working pressure and extreme control in temperature. Cylindrical rollers are used to produce the strips, sheet and plate. In contrast, grooved rollers are employed in producing the rounds and other structural shapes. In sheet and plate rolling process, cross rolling is done to reduce the anisotropy in mechanical properties. Texture strengthening is less

S.No.	Forging type	Features
1	Open-Die Forging	Simple shapes can be made     The previous step to closed – die forging
2	Closed-Die Forging	It is also called an impression die forging     More complex shapes can be obtained
3	Hot-die forging	Die is maintained at a higher temperature compared to open and closed die forging
		• Less energy is required to produce the shape
4	Isothermal Forging	Preheating the metal is required
		• Dies are at the same temperature as the metal
		<ul> <li>Capable of producing near net shape components with less energy required</li> </ul>
5	Precision forging	No machining required before assembling
		Highly sophisticated and expensive method
		• Aero engine fan blades and even aerofoil shapes are precision forged

**Table 1.**Types of forging and its features [1].

pronounced in the beta alloys compared to alpha alloys [1]. The lower rate of strain hardening of the beta alloy makes it more acquiescent to cold working.

In Ti-3.5Al-5Mo-6V-3Cr-2Sn-0.5Fe alloy, rolling and ageing in the sub-transus (alpha + beta field) temperature yielded a better combination of the strength and ductility compared to working in the beta field [13]. Sheet beta Ti alloys are amenable to cold rolling. Cold rolling has a strong effect upon mechanical properties. For example, Rosenberg [14] reported the effect of cold rolling on tensile strength, yield strength and ductility of Ti-15-3 alloy:

- 1. UTS (Rolled alloy) = UTS (un-rolled) +  $0.75 \times Percentage of reduction (%)$
- 2. YS (Rolled alloy) = YS (un-rolled) + 0.65 × Percentage of reduction (%)
- 3. Ductility (Rolled alloy) = EL (un-rolled)  $-0.65 \times Percentage of reduction (%)$

Two high roll mill and three high roll mill are commonly used for rolling titanium and its alloys.

## 2.4 Thermomechanical processing

Material processing performed with the aid of both mechanical force and thermal/ heat treatment can be termed as thermomechanical processing. The primary objective of this processing is to obtain a component in functional design with pre-determined microstructure and corresponding mechanical properties. Thermomechanical processing of beta Ti alloys can be done both above transus temperature (Super-transus processing) and below the transus temperature (Subtransus processing). Super-transus processing with hot deformation is optimised to obtain fine recrystallised beta grains. Sub-transus processing is optimised to obtain fine beta grains with controlled alpha phase morphology [12]. Size, volume fraction, morphology, and the spatial distribution of the alpha precipitates formed during the thermomechanical processing have a vital influence over the mechanical properties of the end product.

In Ti-15V-3Al-3Cr-3Sn alloy, Boyer et al. [15], showed the usefulness of thermomechanical treatment for attaining a wide range of tensile strength (from 1070 to 1610 MPa.)

#### 2.5 Heat treatment

Heat treatment is the basic metallurgical process through which optimization of hardness, tensile strength, fatigue strength and fracture toughness can be achieved. All the metastable beta alloys are heat treatable to attain higher strength than alpha + beta alloys.

Duplex ageing treatment yielded a superior combination of mechanical properties with no precipitation free zone and finer alpha precipitation compared to single ageing in Ti-15V-3Al-3Cr-3Sn-3Zr [16] and Ti-3Al-8V-6Cr-4Mo-4Zr [17]. The rate of heating to ageing temperature was found to have a substantial effect on the evolution of microstructure and mechanical properties [18]. Choice of solution treatment temperature is important. For example, for Ti-1Al-8V-5Fe (Ti185), solution treatment near beta transus temperature leads to a highest tensile and yield strength [19].

Solution treatment followed by ageing in metastable beta alloys will lead to a microstructure consisting of soft alpha in the beta grain boundaries. Hence, this softer alpha phase may lead to the decline in the HCF behaviour [20] and tensile ductility by augmenting the intergranular fracture [17]. For example, Sauer and

Luetjering [21] have also reported the adverse effect of alpha phase layers along the beta grain boundaries on the tensile and fatigue behaviour of Ti-5Al-2Sn-4Zr-4Mo-2Cr-1Fe ( $\beta$  CEZ).

#### 2.6 Surface processing for aerospace application

Modifying the surface is an effective and economical way to enhance the tribological and fatigue properties of the material. Thermo-chemical and mechanical surface modification techniques are common in beta alloys.

#### 2.6.1 Thermo-chemical surface modification

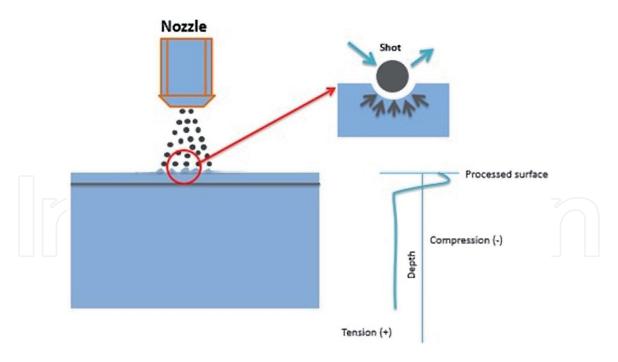
In order to enhance the surface hardness, wear resistance and near-surface strength, thermo-chemical surface processing techniques such as nitriding and carburising are employed. Among various thermo-chemical surface processing techniques, nitriding is extensively used. In this process, the nitrogen is fused into the titanium base alloy. Among the various technologies used for Nitriding, i.e., gas nitriding, laser nitriding, plasma nitriding, Ion nitriding and gas Nitriding are used widely [22]. Titanium nitrides will be formed on the surface as a result of the nitriding and these nitrides increase the surface hardness drastically and improve the tribological properties at the expense of the ductility of the material. Increased hardness due to TiN formation was made use in flap tracks of Military airplanes [23]. However, nitriding has a negative influence on the tensile strength and fatigue strength of the material.

#### 2.6.2 Mechanical surface modification

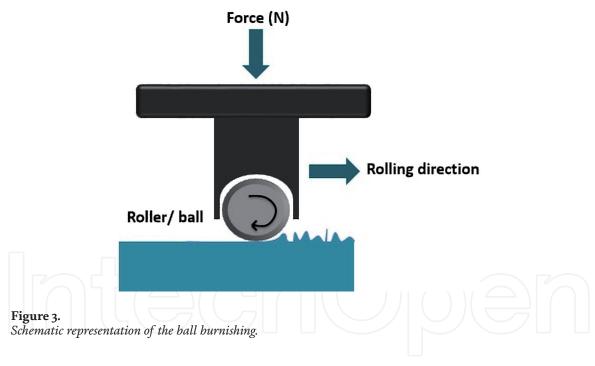
Mechanical surface modifications such as shot peening, ball burnishing and laser peening are developed to enhance the fatigue behaviour of the target material by inducing the residual compressive stress and work hardening effect in near surface region. Both crack nucleation and crack propagation during fatigue loading were found to be affected by the surface modification treatment. However, surface roughness will be significantly increased at the end of the mechanical surface modification such as shot peening and this may lead to early crack initiation.

Since 1970s, shot peening is being employed in enhancing the mechanical behaviour of Ti alloys in aerospace industries [24]. Schematic representation of shot peening is shown in the **Figure 2**. Shot peening of beta alloys, i.e. Ti-10V-2Fe-3Al and Ti-3Al-8V-6Cr-4Mo-4Zr yielded a marginal increase in the fatigue life compared to electro polished sample [25]. In LCB beta alloy, in order to compensate the residual compressive stress induced in the surface after peening, substantial tensile residual stress formed in the subsurface region and this deteriorated the fatigue behaviour compared to polished sample [26]. It is important to control the shot peening conditions to get the desired enhancement in fatigue life.

Unlike shot peening and laser peening, roller burnishing reduces the surface roughness by stressing the surface with a roller ball with optimised pressure. Schematic representation of the roller burnishing is shown in the **Figure 3**. Roller burnishing of Ti-10V-2Fe-3Al beta alloy induced deeper and higher magnitude residual stress compared to shot peening. In roller burnishing of LCB beta alloy, higher the rolling pressure, deeper was the site for fatigue crack nucleation [27]. In Beta C (Ti-3Al-8V-6Cr-4Mo-4Zr) alloy, deep rolling ended up with deeper residual stress distribution compared to shot peening, but the magnitude of the residual stress remained high for the shot peened sample. A marginal increase in fatigue life was achieved through deep rolling of Beta C alloy [28].



**Figure 2.** Schematic representation of shot peening.



Compared to shot peening, laser peening has unique features like the capability of inducing deeper and stable residual stress with extreme control in operation. Conventionally, laser peening is performed using Nd: Glass lasers after applying the coating, i.e. black paint on the target surface. To make this process simple, economical and more portable, LPwC (Laser peening without Coating) was developed in 1995 [29]. LPwC has proven to be an effective technique by inducing a relatively high compressive residual stress. For example, a residual stress of approx. -825 MPa was induced at a depth of  $\sim$ 75  $\mu$ m from the surface in LCB (Ti-6.8Mo-4.5Fe-1.6Al) beta alloy [30].

#### 2.7 Surface processing for bio-medical application

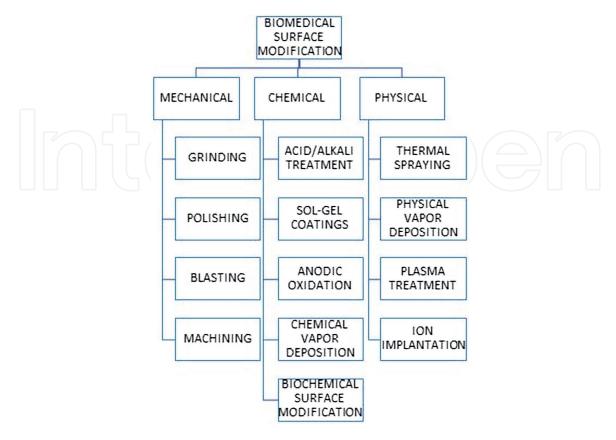
In the case of implant materials, the interaction between the biological environment and the implanted materials occurs on the biomaterial surface. Clinical

success of implant materials is greatly dependent on various surface characteristics viz. chemical inertness, texture, corrosion resistance and surface energy [31] . In the case of orthopaedic implants, the surface should possess more bone forming ability and for blood contacting devices, it should not initiate any blood clot formation. Hence surface modification of biomedical grade beta titanium alloys is very significant. Oxide layer formation will occur spontaneously on the surface of titanium on exposure to air. This  $\text{TiO}_2$  film possesses a thickness of about 1.5 to 10 nm at room temperature. Chemical stability and structural characteristics of this oxide film greatly influence the biocompatibility of titanium implant materials. Some of the potential methods to enhance the properties of native  $\text{TiO}_2$  film are anodisation, sol–gel methods, acidic and alkaline treatments [32]. In addition to these, specific surface topographies and roughness induced by mechanical surface modifications (sandblasting, grit blasting, peening) have improved the clinical success of implant materials. An overview of the various surface modification techniques employed for biomedical beta titanium alloys is schematically shown in Figure 4.

In dental applications, Laser Nitriding has proved to be an effective process in enhancing the surface hardness, the coefficient of friction and corrosion resistance of the Ti-20Nb-13Zr and wear and corrosion resistance of Ti-13Nb-13Zr biomedical-beta alloys [34, 35]. Plasma nitrided beta 21S (Ti-15Mo-3Nb-3Al-0.2Si) alloy showed higher hardness but inferior corrosion resistance compared to the untreated alloy [36]. In line with the Nitriding, carburising of Ti-13Nb-13Zr (a biomedical beta alloy used for artificial joints) improved the surface hardness and wear resistance through the formation of the titanium carbide [37].

#### 2.8 Powder metallurgy

As mentioned in the introduction (Section 1), a major limiting factor for the titanium application is its high production cost. In addition to the high raw



**Figure 4.**Overview of surface modification of beta titanium alloys for biomedical application [33].

material cost, the forging, machining contribute majorly to the production cost. This limitation instigated the industries to work towards processing methods through which the near net shape (NNS) could be obtained. Despite the higher cost involved, Powder metallurgy of titanium is capable of yielding almost same or better mechanical properties compared to wrought and cast components along with accurate net shape capability. This merit is mainly attributed to the absence of texture, segregation and nonuniformity in the grain size encountered in conventional processing.

Even for the components made through powder metallurgy route, solution treatment followed by ageing (STA) leads to an enhancement in mechanical properties such as tensile strength and yield strength compared to the as-sintered condition [38]. Ti-10V-2Fe-3Al and Ti-11.5Mo-6Zr-4.5Sn alloys have been produced through powder metallurgy route. However, 90% of the powder metallurgy is focussed on the alpha + beta alloy Ti-6Al-4V.

Guo et al. [39] reported a remarkable increase in the mechanical properties of Ti-10V-2Fe-3Al powder alloy compared to the wrought and cast products through isothermal forging of the sintered alloy. Jiao et al. [40] studied the model of alpha phase spatial distribution in laser additive manufactured Ti-10V-2Fe-3Al. The influence of nano-scale alpha precipitates on tensile properties of age hardened laser additive manufactured Ti-5Al-5Mo-5V-1Cr-1Fe (Ti-55,511) alloy was studied by He et al. [41] and the authors reported that precipitated nanoscale alpha precipitates have led to a decline in ductility.

# 3. Applications

#### 3.1 Aerospace applications

A recent forecast released by Airbus Industries [42], confirms the promising development of air transport requiring 37,400 aircraft at a value of 5.8 trillion US dollars business in the next 20 years. However, reducing the fuel consumption to control the emission of  $\rm CO_2$  and  $\rm NO_x$  is the driving factor for the aerospace industries and this could be possible by reducing the overall weight [43]. Similarly, in space application weight of the payload is more crucial than civil/cargo aviation. Ti-6Al-4V is a workhorse for the aerospace industry for several decades and 65% of total titanium production in the United States belongs to Ti-6Al-4V alloy [3]. Even though the alpha +beta alloys dominated the scene, beta alloys with their unique characteristics such as excellent hardenability, heat treatability to high strength levels and a high degree of sheet formability, are becoming increasingly important for the aerospace sector. Beta alloys and their aerospace application are listed in the **Table 2**.

#### 3.2 Biomedical applications

Titanium is the ultimate choice for biomedical applications as they outperform conventionally used biomedical alloys such as 316L stainless steel and cobalt-chromium alloys [47]. The formation of a nanometre thick oxide layer on titanium when exposed to any environment imparts high corrosion resistance and superior biocompatibility [48]. All classes of titanium  $\alpha$ ,  $\alpha + \beta$ , near  $\beta$  and  $\beta$  alloys are widely used for biomedical applications.

Despite being initially developed for aerospace applications, CP titanium and Ti-6Al-4V are still the most widely used Ti grades being used for biomedical applications. However, CP Ti is associated with lower wear resistance and Ti-6Al-4V when implanted inside the body releases Al and V ions which can

S. No.	Alloy	Application/components
1	Ti-15V-3Al-3Cr-3Sn	Landing gear, springs, sheet, plate and airframe castings, environmental control system ducting
2	Ti-6V-6Mo-5.7Fe-2.7Al	Fasteners
3	Ti-13V-11Cr-3Al	Airframe, landing gear and springs
4	Ti-3Al-8V-6Cr-4Mo- 4Zr (β-C)	Springs and fasteners
5	Ti-11.5Mo-6Zr-4.5Sn	Rivbolts—Boeing 747
6	Ti-5Al-5Mo-5V-3Cr	Aircraft landing gear, Fuselage components and high lift devices
7	Ti-10V-2Fe-3Al	Aircraft landing gear     High strength forging
8	Beta 21s	1. Nozzle assembly parts in Boeing 777 2. Planned to use in Pratt & Whitney PW4168 engine component
9	Ti-35V-15Cr (Alloy C)	Compressor and exhaust nozzle components

**Table 2.**Aerospace applications of beta titanium alloys [4, 9, 17, 43–46].

lead to severe neurological disorders and allergic reactions. Moreover, the elastic modulus values of these alloys (~110 GPa) are almost four times than that of human cortical bone (20–30 GPa) which can lead to stress shielding effect. This led to the development of  $\beta$ -Ti alloys composed of non-toxic elements and their inherent lower elastic modulus assists in reducing the stress shielding effect when used for orthopaedic applications [3]. Alloy systems based on Ti-Nb, Ti-Mo, Ti-Ta and Ti-Zr are potential materials for biomedical applications. Some of these  $\beta$ -Ti alloys initially developed are Ti-15Mo-5Zr-3Al, Ti-12Mo-6Zr-2Fe (TMZF), Ti-15Mo-3Nb-0.3O (21SRx) and Ti-13Nb-13Zr possessing modulus values in the range of 70–90 GPa.

In the early 1990s, medical device industry focused on developing these low modulus  $\beta$ -Ti alloys for orthopaedic applications. Initially, two  $\beta$ -Ti alloys Ti-13Nb-13Zr specified by ASTM F1713 and Ti-12Mo-6Zr-2Fe (TMZF) specified by ASTM F1813 received Food and Drug Administration approval as implant materials. Among these, TMZF alloy possesses an elastic modulus of about 74–85 GPa, with a yield strength of 1000 MPa. During the early 2000s, this metastable  $\beta$ -Ti alloy was used for making hip stems, which rub against a modular neck made from a cobalt-chromium based alloy. However, in 2011, the US Food and Drug Administration recalled the use of this TMZF alloy due to the unacceptable level of wear debris formation. Another  $\beta$ -Ti alloy 21SRx is derived from the aerospace alloy 21S from which aluminium was eliminated over biocompatibility concerns. In addition, alloys such as Ti-29Nb-13Ta-4.6Zr and Ti-35Nb-7Zr-5Ta are receiving increasing attention due to their lower elastic moduli of about 65 and 55 GPa, respectively, lower than other  $\beta$ -Ti alloys [50].

Apart from orthopaedics, titanium is extensively used in the dental applications [49]. In the case of orthodontic wire material, it should possess three general characteristics viz. large spring back (ability to be deflected over longer distances without permanent deformation), lower stiffness and high formability [51]. The initially utilised materials for orthodontic wire application were gold based alloys containing copper, palladium, platinum or nickel. However, spring back values of these gold alloys were limited owing to their lower yield strength. In the 1960s gold was replaced by stainless steel and cobalt-chromium based alloy (elgiloy). These materials continue to be the standard orthodontic wire material for the past

70 years and possess higher springiness and strength with comparable corrosion resistance. During the early 1970s, nickel-titanium alloy Nitinol (Nickel Titanium Naval Ordinance Laboratory) was also used for orthodontic wires. Even though Nitinol orthodontic archwires are widely used owing to their superior superelastic properties, their use is hampered by reduced formability during the final stages of treatment. Moreover, there are serious concerns over the nickel ion release from these materials in the oral environment. It was later demonstrated that orthodontic wires made from β-Ti alloy Ti-11,3Mo-6,6Zr-4,3Sn (TMA alloy) possess enhanced spring back and formability, along with reduced stiffness. TMA alloys possess ideal elastic modulus values lower than that of stainless steels and higher than nitinol [51]. The higher surface roughness associated with these TMA wires can, however, lead to arch wire-bracket sliding friction due to the high coefficient of friction of TMA alloys. One of the most successful approaches to tackle this problem is the ion implantation process which renders the TMA wires with lower surface roughness and reduced friction coefficients. Another beta titanium alloy Ti-6Mo-4Sn was also investigated for orthodontic wire applications. By proper heat treatment procedures, this alloy exhibited an elastic modulus of 75 GPa and a tensile strength of 1650 MPa [52]. Ti-13V-11Cr-3Al, metastable Ti-3Al-8V-6Cr-4Mo-4Zr, metastable Ti-15V-3Cr-3Al-3Sn, near-beta Ti-10V-2Fe-3Al were also researched for dental archwire applications.

Though beta titanium alloys possess superior haemocompatibility, which is beneficial for cardiovascular devices, they are not fully exploited for cardiovascular applications. Despite higher haemocompatibility, no  $\beta$ -Ti alloy based stents have been commercialised which can be attributed to their lower ductility and modulus as compared to 316L stainless steel and cobalt-chromium based stent materials. Recently, research based on the development of new  $\beta$ -Ti alloy compositions for coronary stent applications has been getting increased attention. Initial studies on Ti-12Mo (wt %) and ternary Ti-9Mo-6W (wt %) demonstrated a ductility of about 46% and 43% respectively [53]. Apart from this, initial investigations on Ti-50Ta, Ti-45Ta-5Ir and Ti-17Ir for stent applications were performed by Brien et al. [54]. Among the three alloys, Ti-17Ir exhibited a favourable elastic modulus of 128 GPa owing to the eutectoid Ti3Ir phase precipitation; iridium content will also assist in improving the fluoroscopic visibility of the stents during interventional procedures [54].

#### 4. Conclusions

Beta titanium alloys have shown much promise and extensive research and development work has been devoted to this group of alloys over the last four decades. For aerospace applications, their heat treatability, high hardenability, high strength to weight ratio and excellent hot and cold workability are major attractions. For orthopaedic applications, their corrosion resistance to biofluids, biocompatibility and low elastic modulus coming close to that of human bone are the important attractive features. Accordingly, development of cost-effective processing techniques has also assumed importance. Problems unique to beta titanium alloys such as high degree of proneness to segregation, high loads to be applied during hot working etc. have since been resolved. Powder processing and additive manufacturing of the alloys have recently received attention and hold promise. Surface modification has been an important part of the developmental efforts and has taken a prominent place, especially for biomedical applications. Coming years are bound to witness increased exploitation of this group of alloys, particularly in biomedical and aerospace applications.

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#### **Conflict of interest**

The authors declare that there is no conflict of interest regarding the publication of this article.

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