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Beta Titanium Alloys: The Lowest Elastic Modulus for Biomedical Applications: A Review

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***Abstract*—**Biometallic materials are the most important materials for use in biomedical applications especially in manufacturing a variety of biological artificial replacements in a modern worlds, e.g. hip, knee or shoulder joints, due to their advanced characteristics. Titanium (Ti) and its alloys are used extensively in biomedical applications based on their high specific strength and excellent corrosion resistance. Beta-Ti alloys containing completely biocompatible elements are exceptionally prospective materials for manufacturing of bioimplants. They have superior mechanical, chemical and electrochemical properties for use as biomaterials. These biomaterials have the ability to introduce the most important property of biochemical compatibility which is low elastic modulus. This review examines current information on the recent developments in alloying elements leading to improvements of beta Ti alloys for use as biomaterials. Moreover, this paper focuses mainly on the evolution, evaluation and development of the modulus of elasticity as an effective factor on the performance of beta alloys.

***Keywords*—**Beta Alloys, Biomedical Applications, Titanium Alloys, Young's Modulus.

I. INTRODUCTION

OVER the previous decade there has been a significant impact of metallic implant materials such as stainless steels, cobalt-chromium based alloys and titanium (Ti) based biomaterials especially in applications requiring mechanical properties. Even today, among metallic materials, Ti and its alloys are extensively used in a variety of applications like aerospace, chemical industries, power plants, medical prostheses [1] due to their good mechanical properties and corrosion resistance [2]. They are considered to be the best choice for replacing or repairing failed hard tissues (structural biomedical applications) as these materials present excellent biocompatibility, high strength to density ratio, outstanding corrosion resistance due to an oxide layer formation on surface, as well as low modulus of elasticity that is closer to bones than biomedical stainless steels and cobalt-chromium alloys, thereby decreasing risk of catastrophic failure during prostheses service life [3]-[6].

The α+β type Ti–6Al–4V alloy (ASTM F1108) has been used as structural biomaterial for manufacturing orthopedic prostheses and dental implants because of its excellent specific strength, corrosion resistance, and biocompatibility characteristics [7]. However, the alloying elements present in this alloy have their own adverse effect in biomedical environment. The literature also exhibits that the presence of vanadium (V) ions into human tissues can alter the kinetics of the enzyme activity associated with the inflammatory response cells [8], [9]. Presence of aluminum (Al), on the other hand, increases the potential for the development of Alzheimer's disease [10] especially during long-term implantation. Additionally, one of the most important properties which puts serious limitations on the performance of Ti alloys as implant materials for artificial joints (e.g. hip, knee or shoulder joints etc.) is its higher modulus of elasticity. It is essential that the stiffness of the implant material be as close as possible to the connected bone. This characteristic facilitates an effective transfer of mechanical stress, by providing stress shielding effect, through the interface from the implant to the adjacent bone and avoids the damage of bone cells [11]. When there is a large different between the stiffness of the two, it may cause osteoporosis or poor osseointergration (poor bone–Ti implant contact integration) [12] which may, consequently, lead to crack nucleation and an eventual failure of the implant [13]. Ti-6Al-4V alloy has a modulus of approximately 110 GPa [14], which is extensively higher than that of human bone (10-40 GPa) [15]. The high modulus of Ti-6Al-4V is as a result of high amount of Al content which leads to increase in volume fraction of α phase [2].

Recently, β-type Ti alloys containing Nb, Zr, Ta, Mo, Sn, etc. have attracted considerable attention especially for orthopedic implants applications owing to their unique combination of better mechanical properties, low elastic modulus, superior biocorrosion resistance, no allergic problems, and excellent biocompatibility. It is found that their elastic modulus can be significantly reduced by adjusting the concentration of β stabilizing elements [16]-[18]. Moreover, this type of Ti alloys exhibits extraordinary corrosion resistance in human body fluid. This behavior is due to the formation of a protective, hard and tightly adherent oxide film [19]. Therefore, Ti-based alloys with above nontoxic and non-allergic elements and other elements have been widely used to design new β-type Ti alloys [20]. In this regard, the addition of β stabilizing elements is preferred to develop absolutely safe Ti-based alloys for biomedical applications depending

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upon its ability to achieve biological passivity and capacity of reducing the elastic modulus [21].

Extensive studies in terms of hard work and focus have been dedicated by engineers and materials scientists for development of β-Ti alloys for various biomedical applications with superior required properties. The importance of the subject, increasing research interest and huge unexplored potential is the driving force behind this literature review. The present review study has been done with a view to provide the researchers in the field to have a bird's eye view on the hotspots on research in the field of biomedical Ti alloys.

II. THE CRITERIA OF SELECTION IMPLANTABLE METALS

The field of biomedical titanium materials is one of the fastest growing areas of research for the contemporary materials scientist and engineers, as these materials can enhance the fineness and longevity of human life, and ameliorate patient health care. The development of titanium materials for biomedical applications is currently an area of active research around the globe and many serious attempts are made every year to improve different desirable requirements in this field.

As the load-bearing applications like hip and joint replacements are a complex and dynamic field, various requirements must be fulfilled. Design engineers and orthopedics must consider the physiological loads to be placed on the implants and combine all the requirements for sufficient structural integrity to facilitate a person's life normal and painless. Hence, the selection of a biometals to be employed as a load-bearing orthopedic device should be based on a reliable analysis of relevant materials properties. In short, the most important requirements for any metal to be successful as implant in human body may be lined as following:

1. Outstanding biocompatibility.
2. Better osseointegration (bone ingrowth).
3. Improved mechanical properties such as specific strength, fatigue resistance, impact strength, ductility and low young's modulus.
4. Superior corrosion behavior in body fluid.
5. Encouraging tribological characteristics such as low friction and high wear resistance.
6. Long term dimensional stability.
7. Processability (casting, plastic deformation, powder metallurgy, machinability, and welding).

III. ALLOYING SYSTEMS OF BIOMEDICAL BETA TITANIUM ALLOYS

In general, Ti alloys may be classified as Alpha (α), near-α, Alpha-Beta (α-β), metastable β, and stable β depending upon the microstructure at room temperature. In this regard, alloying elements for Ti fall into three categories: (1) α-stabilizers, such as Al, O, N, C; (2) β-stabilizers, such as V, Nb, Ta, Mo (isomorphous), Fe, W,Cr, Ni, Si, Co, Mn, H (eutectoid); (3) neutrals, such as Zr and Sn [22]. The α and near-α Ti alloys exhibit superior corrosion resistance but have limited low temperature strength. In contrast, the α + β alloys exhibit higher strength due to the presence of both the α and β phases.

The β alloys also offer the unique characteristic of low elastic modulus and superior corrosion resistance [23], [24]. Earlier systems of Ti in medical, surgical, and dental devices were based on commercially pure Ti (cpTi) and most popular used Ti-6Al-4V alloy. As a result of the fact that releasing small amounts of vanadium and aluminum in the human body induces possible cytotoxic effect and neurological disorders, respectively [25]-[28] led to develop Ti-6Al-7Nb [26], Ti-Zr based and Ti-Sn based alloys [29].

The new generation β-type Ti alloys with non-toxic elements systems have been developed recently such as:

(a) Binary systems

Ti-Nb system [30], Ti-Mo system [31], [32], Ti-Ta system [33], Ti-Zr system [34], Ti-Mn system [35], Ti–Cr system [36], [37];

(b) Ternary systems

Ti-Nb-Mo system [38], Ti-Nb-Pd system [39], Ti-Nb-Zr system [40]-[43], Ti-Nb-Sn system [44], Ti-Nb-Ta system [45], [46], Ti-Nb-Fe [47], Ti-Mo-Zr system [48], Ti-Mo-Nb system [49], Ti-Cr-Al system [50], [51], Ti–Cr–Nb system [52], Ti-Cr-Sn system [53], Ti–Mn–Al [54], Ti-Ta-Nb system [55], Ti-Ta-Sn system and Ti-Ta-Zr system [56], Ti–Mn–Fe [57], Ti–Sn–Cr [58];

(c) Quaternary systems

Ti-Ta-Sn-Zr system [59], Ti-Nb-Zr-Sn system [60], [61], Ti-Nb-Zr-Fe system [62], Ti-Nb-Ta-Zr system [63]-[65], Ti-Mo-Zr-Fe system [66], Ti-Fe-Ta-Zr system [67], Ti-Cr-Mn-Sn system [68], and other systems are still evolving.

IV. MODULUS OF ELASTICITY PROPERTY AND ITS RECENT DEVELOPMENTS

Elastic modulus is an imperative physical property for Implantable materials which is quite relevant to various replacements as artificial hip joints, bone plate and gum implants. This is because a "stress shielding effect" will result in the reabsorption of natural bone and the implant loosening if great difference of elastic modulus exists in between hard tissue replacement and human bone.

Generally, metallic implants possess a much higher elastic modulus and their linear stress–strain characteristics do not match the plateau-like hysteretic behavior of bones, which leads to an implant loosening and finally leading to its failure. Hence, for use as worn or damaged bone replacements, the required mechanical properties of a biocompatible material must be as close as possible to those of bone, especially the Young's modulus. The modulus of elasticity is one of the most common affected properties on performance of Ti as implantable materials for artificial joints, e.g. hip, knee or shoulder joints. It is well known that Young's modulus is determined by the bonding force among atoms and greatly affected by the crystal structure. So, extensive studies and serious attempts were made in recent past to achieve better performance (lower E) in terms of biomechanics, as given in Table I.

TABLE I
DIFFERENT ELASTIC MODULUS VALUES OF VARIOUS MEDICAL TITANIUM MATERIALS

Alloy Designation	Type alloy	E (Gpa)
Ti-19Nb-14Zr	Near β	14
Ti–24Nb–4Zr–7.9Sn	β	33
Ti-29Nb-6Ta-5Zr	β	43
Ti-35Nb-4Sn	β	44
Ti35Nb2Ta3Zr	β	<50
Ti-10Zr-5Ta-5Nb	β	51.97
Ti–(18-20)Nb–(5-6)Zr	Near β	45-55
Ti-25Ta-25Nb	β	55
Ti-29Nb-13Ta-7.1Zr	β	55
Ti-35Nb-7Zr-5Ta	Near β	55
Ti–35Nb–5.7Ta–7.2Zr	β	57
Ti-28Nb-13Zr-2Fe	Near β	58
Ti–28Nb–13Zr–0.5Fe	Near β	58
Ti-29Nb-11Ta-5Zr	β	60
Ti-29Nb-13Ta-2Sn	β	62
Ti-12Mo-5Zr	β	64
Ti-29Nb-13Ta-4.5Zr	β	65
Ti–25Nb–2Mo–4Sn	Near β	65
Ti-29Nb-13Ta-4.6Sn	β	66
Ti–35Nb–5Ta–7Zr–0.40	β	66
TLM Alloy	β	67
Ti–12Mo–5Ta	Near β	74
Ti-29Nb-13Ta-4Mo	β	74
Ti-29Nb-13Ta-6Sn	β	74
Ti-12Mo-6Zr-2Fe	β	74-85
Ti-13Nb-13Zr	Near β	77
Ti-15Mo	β	78
Ti-15Mo-2.8Nb-3Al	Near β	82
Ti-7.5Mo-3Fe	β	85

V. INFLUENCE OF DIFFERENT FACTORS ON THE MODULUS OF ELASTICITY IN BETA TI ALLOYS

As mentioned in previous sections, selection of non-toxic elements that have ability to stabilize β phase affects the stiffness values of Ti alloys significantly as shown in Table I.

The beta stabilizers can be categorized into three groups [69]:

1. Elements that are isomorphous to β-Ti and form continuous solid solutions with limited solubility in α-phase: Ta, Nb, V and Mo;
2. Elements that form continuous solid solutions in α- and β-Ti: Zr and Hf; and
3. Elements with a limited solubility in both α- and β-Ti which form intermetallic compounds: Mn, Cr, Fe, Cu, Ni, Si, and Co.

In addition to optimisation of alloy compositions, many different faclose packed (hcp) α pctors can result in decreasing the elastic modulus. One of the main parameters that affects the elastic modulus of β-Ti alloys is microstructural features that is governed by the amount and type of alloying elements and the processing routes employed. In fact, the elastic modulus of the body centered cubic (bcc) β phase is lower than that of the hexagonal hase. Yao et al. [70] found that β phase had the lowest Young’s modulus, which was 35.29 GPa compared to the other phases which may be formed in Ti alloys. Therefore, a number of β-type Ti alloys mainly composed of toxicity-and-allergy-free elements especially above mentioned elements and with low Young’s moduli have been developed and are still being developed [71]. Extensive studies and serious attempts were made in recent past to achieve better performance (lower E) in terms of biomechanics via changing microstructural features For example, It is reported that the presence of martensite phase in the microstructure of Ti-30Ta alloy produced a good combination of low modulus and high strength [33], [72]. Recently, Brailovski et al. [69] proved the minima in Young's modulus of metastable β-alloys TiNbZr(Ta) as a result of stress-induced martensitic transformation. They established the goals of stabilizing the β phase at room temperature, to create conditions of α″ phase formation, to decrease Young modulus, and to promote solid solution hardening.

The thermo-mechanical Processing (TMP) is also a very important means to decrease the Young’s modulus of β-base Ti alloys. Bertrand et al. [73] pointed out a very low Young's modulus for Ti-25Ta-25Nb alloy that lies at 55 GPa (which is one of the lowest values for a β-Ti alloy) by performing thermo-mechanical processing. TMP included cold rolling at 80% and solution treatment at 850 ^{0}C for 0.5 h in the β phase field and water quenched. The aim of this treatment was to restore a fully recrystallised β phase microstructure from the cold rolled state with a reduced β grain size which in turn provides low value of Young's modulus.

Omega (ω) phase is a metastable phase in Ti-based alloys with hexagonal structure. In general, it is important to suppress the deleterious and harmful precipitation of omega (ω) phase which increases strength and improves superelastic property at the expense of the value of elastic modulus. The elastic modulus increases with increasing the volume fraction of ω phase as the Young’s modulus of ω phase is higher than that of β and martensite phases [74]. Hsueh-Chuan et al. [75] investigated the effects of Fe on the structure and mechanical properties of a Ti–5Nb based alloy in order to gauge the potential of new alloys for practical biomedical applications. They reported that the highest bending modulus was associated with the formation of the largest quantity of ω phase formed during quenching in the Ti–5Nb–3Fe alloy.

Heat treatment is one of the most often used methods that can suitably adapt the Young’s modulus of Ti alloys. Solution treatment, sometimes, leads to excellent matching of moduli of elasticity because of resultant phases as shown by Changli Zhaoa et al. [76]. They have investigated a Ti–12Mo–5Zr alloy which exhibited acicular martensitic phase plus beta phase structure with lower Young’s modulus (about 64 GPa) after solution treatment which showed better mechanical biocompatibility.

Aging treatment is an effective method to develop static and dynamic strength by precipitation hardening by simultaneously introducing secondary phases such as α and ω

within the β matrix of Ti alloys. However, the Young's modulus rises to a value similar to that of Ti–6Al–4V ELI, although the control of aging treatment allows the Young's modulus to be kept below 80 GPa, which is close to the highest value among β-type Ti alloys, but is still lower than that of (α+ β)-type Ti alloys. Hence, short aging develops the fatigue strength of β-type Ti alloys while the Young's modulus is kept below 80 GPa [77]. Miinomi [78] demonstrated through his research on Ti–29Nb–13Ta–4.6Zr β-type alloy that the aging treatment at 673K for 259.2 ks after solution treatment at 1063K for 3.6 ks can achieve precipitated phases distributed homogeneously over the whole material, and they are α phase, a small amount of ω phase, and β phase. Young's modulus of Ti alloy has been reduced as a result of these microstructural changes and reaches to (65 Gpa) which is much lower than that of Ti-6Al-4V ELI Alloy. Recently, Shun Guo, et al. [79] carried out a systematic study and investigated microstructure evolution and mechanical behavior of a metastable β-type Ti–25Nb– 2Mo–4Sn (wt%) alloy with high strength and low modulus. They obtained superior mechanical properties, i.e. high ultimate tensile strength of ~1113 MPa and low elastic modulus of ~65 GPa by cold rolling coupled with short-time aging treatment. They reported that the precipitation of fine α by short-time aging did not cause the enrichment of β- stabilizers in β matrix, guaranteeing low elastic modulus of the short-time aged specimen. Moreover, fine α precipitates as well as dislocations were reported to have played a crucial role in strengthening, giving rise to its high yield strength and high ultimate tensile strength.

The elastic modulus of β-Ti alloys is an anisotropic parameter and strongly depends on the crystal orientation. Further, the Young's modulus of β-type Ti alloys decreases depending on the manner of processing performed to control the crystallographic texture. Tane et al. [80] found that a single crystal of the low modulus β-type TNTZ alloy oriented in the ⟨100⟩ direction showed a lower Young's modulus (35 GPa) than those oriented in other directions, such as ⟨111⟩ and ⟨110⟩. Recently, WenFang et al. [81] investigated the texture evolution of a biomedical β-Ti alloy (Ti-28Nb-13Zr-2Fe) under 15%–85% cold rolling and 700°C–900°C recrystallization annealing treatment, and discussed the effects of crystal orientation on Young's modulus of the alloy. The Young's modulus exhibited the lowest value (54 GPa) under 15% reduction. Strong {111}⟨112⟩ γ-fiber texture was developed after rolling (85% reduction) and annealing at 700°C, which was favorable to decreasing Young's modulus in comparison with randomly orientated microstructure. They confirmed that the gradual rotation of {110} slip plane during plastic deformation promoted the development of {001}⟨110⟩ texture component, leading to the marked decrease of Young's modulus.

In order that a living bone attaches itself permanently to an implant, an artificial bone should have a porous structure. It has been established that porous Ti implants are important to promote tissue in-growth and in the firmly securing of an implant [82]. Several manufacturing techniques are capable of producing porous materials, such as sintering, self-propagating or combustion synthesis (SHS), freeform fabrication, etc. Some recent studies show the potential of using these techniques to control pore size, shape, orientation and distribution, including the creation of hierarchical and functionally-graded pore structures [83], [84]. Compression testing of the porous Ti–(18-20)Nb–(5-6)Zr alloy as a function of porosity (from ~45 to 66%) and interconnected cell size (d_{50} from 300 to 760 μm) has been performed by Brailovski et al. [69]. Their results revealed that the Young's modulus of the porous samples varied from 7.5 to 3.7 GPa, depending on the porosity, which is close to that of trabecular bones.

VI. CONCLUSION

Extensive use of Ti and its alloys as biomaterials is ubiquitous owing to their specific characteristics especially higher biocompatibility, superior corrosion behavior and lower modulus of elasticity compared to other conventional biomaterials such as stainless steels, cobalt-based alloys, polymers, and composite materials. Novel β-Ti alloys free from toxic alloying elements and with relatively low elastic modulus have recently been developed and received great attention in the biomaterial scientists' community. The merit of increasing use of β-Ti alloys as implantable materials lies, among other factors, in their low modulus of elasticity as well as their other significant properties. In order to obtain lower elastic modulus, recently, the researchers of biomedical Ti alloys focused on β-type Ti alloys that contain non-toxic elements such as Nb, Zr, Ta, Mo, Sn, Cr, Fe, etc. There is an important role of precipitates, texture orientation and porosity obtained, to develop desirable bio-compatible Young's modulus, through various processing techniques. The literature reveals that serious attempts from researchers have been made towards improving function and lifetime of an implant in the human body by reducing significantly the elastic modulus of the biomaterial.

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