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Development of Ti–Nb–Zr alloys with high elastic admissible strain for temporary orthopedic devices

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ABSTRACT

A new series of beta Ti–Nb–Zr (TNZ) alloys with considerable plastic deformation ability during compression test, high elastic admissible strain, and excellent cytocompatibility have been developed for removable bone tissue implant applications. TNZ alloys with nominal compositions of Ti–34Nb–25Zr, Ti–30Nb–32Zr, Ti–28Nb–35.4Zr and Ti–24.8Nb–40.7Zr (wt.% hereafter) were fabricated using the cold-crucible levitation technique, and the effects of alloying element content on their microstructures, mechanical properties (tensile strength, yield strength, compressive yield strength, Young's modulus, elastic energy, toughness, and micro-hardness), and cytocompatibilities were investigated and compared. Microstructural examinations revealed that the TNZ alloys consisted of β phase. The alloy samples displayed excellent ductility with no cracking, or fracturing during compression tests. Their tensile strength, Young's modulus, elongation at rupture, and elastic admissible strain were measured in the ranges of 704–839 MPa, 62–65 GPa, 9.9–14.8% and 1.08–1.31%, respectively. The tensile strength, Young's modulus and elongation at rupture of the Ti–34Nb–25Zr alloy were measured as 839 ± 31.8 MPa, 62 ± 3.6 GPa, and 14.8 ± 1.6%, respectively; this alloy exhibited the elastic admissible strain of approximately 1.31%. Cytocompatibility tests indicated that the cell viability ratios (CVR) of the alloys are greater than those of the control group; thus the TNZ alloys possess excellent cytocompatibility.

1. Introduction

According to a report by the United Nations in 2013 [1], the population of the age group 60 years and older is increasing rapidly, and in the more developed regions of the world, the ratio of elderly people is expected to increase by 45% as of 2050. Orthopedic biomaterials are implanted into human bodies in order to heal bone tissue diseases developed due to aging, various congenital defects in bone tissue, injuries to bone tissue and joints from traffic and sports accidents [2,3].

With the increasing utilization of orthopedic implant materials, if biologically and mechanically compatible materials are not used for implants, it is inevitable that the number of revision surgeries will increase [4]. Genotoxic, cytotoxic, carcinogenic, mutagenic, allergenic, neurological effects are taken into account while evaluating the biological compatibility of an implant material [5]. The formation of stress shielding may occur in cases where an implant material with a higher Young's modulus than that of bone tissue is used [6]. Resorption in bone tissue can occur when it carries lower amounts of biological load due to a rigid implant material carrying most of the loads [7]. In such cases, the implant material may loosen [6]. The fact that titanium (Ti) alloys have a lower Young's modulus in comparison with 316L stainless steel and Co–Cr alloys is an important factor in their increasing use as implant materials [3].

Since Young's modulus of the $(\alpha + \beta)$ Ti–6Al–4V alloy (at 110 GPa) [8] is about 4 times greater than that of cortical bone tissue (max. 27 GPa) [9], β Ti alloys with a relatively lower Young's modulus in comparison with $\alpha + \beta$ Ti alloys have been developed for orthopedic implant applications [10–16]. As it is well known, among the Ti alloys, Ti–6Al–4V is still the most used one for orthopedic applications, even though it contains vanadium, which is defined as toxic [17], as well as having aluminum, for which neurological side-effects [18], and genotoxic effects [19] have been

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reported. Another important consideration is that the cold-forming capabilities of β Ti alloys (e.g. Ti–15Mo–5Zr–3Al) are much better in comparison with α + β Ti alloys (e.g. Ti–6Al–4V) [20]. The superior cold-forming ability of β Ti alloys decreases the manufacturing cost, thus creating an advantage for them in becoming commercial products [4].

The role of Ca–P formations on implant's surface is to accelerate the assimilation of implant material and bone-tissue [21]. For instance, on the surface of bio-inert Zirconia, calcium phosphate formation enabling a chemical bond with the surrounding bone-tissue does not occur, it only ensures morphological fixation while staying in the body [22]. Ca–P formations enable a tight bond between the implant and surrounding bone-tissue [23]. On the other hand, it is crucial to prevent the formation of fibrous tissue between the bone-tissue and implants [24]. A direct contact without fibrosis tissue between implant material and bone is defined as osseointegration. [24]. Implants may be isolated due to fibrous tissue formed between the bone tissue and implant [25]. It is beyond doubt that fibrous tissue formation between the implant and surrounding tissue is not desired, it is a prerequisite for both temporary and permanent implant materials. Unlike osseointegration, chemical bonding between implant and bone tissue is related to calcium phosphate forming ability of implants [26]. The fast formation of fixation between the implant material and bone is provided by calcium phosphate precipitates on the surface of the implant material, which thereby increases bone conduction [27]. Methods such as alkaline treatment [28], micro-arc oxidation [29] and sol–gel [30] are used in order to enhance the adherence of the implant material to the bone tissue or, in other words, to increase chemical bonding ability by providing calcium phosphate formation on the surface. Permanent implants (e.g. artificial joints and dental implants) should have an assimilation ability with bone tissue when assessed on the basis of clinic needs [31]. It is expected that such an implant should offer excellent bioactivity [32]. It is well known that artificial joints take on the natural joint function by replacing the severely damaged joint. It is crucial to introduce artificial joints having the ability of assimilation with bone tissue which ensures patients to carry out daily activities properly for the rest of their lives [33]. When viewed under this aspect, the bone conductivity of permanent implant materials should be high [31].

However, the reverse is required in removable implant applications [34]; that is, calcium phosphate precipitates are undesirable on the surface of removable implants so as to minimize the bone conductance of the implant material, and to prevent assimilation between the bone tissue and the implant material [27]. Contrary to permanent implants, the bonding between implant and bone should be weak enough to prevent refracture of the bone during removal surgery [35]. Trauma implants, e.g. bone nails, lose their function after a healing period and they are removed after fracture union [36]. Unlike artificial joints, trauma implants (e.g. bone nails) do not lead to any restriction of movement function when removed from the body at an assigned time after healing period of the bone tissue, i.e., it is not necessary to remain in the body permanently as artificial joints. Because of the tendency of calcium phosphate precipitation on the surface of some Ti alloys, assimilation occurs between the bone tissue and the implant material which makes them unadaptable as a choice of temporary implants [31]. It is crucial to avoid assimilation of these devices with bone tissue for an easy removal surgery [37]. In cases where there is no assimilation between bone and implant material, the occurrence of new bone fractures during surgery to remove the implant material is minimized, and so the removal surgery is easier [34]. Implant removal becomes necessary with patient demands and complaints [38]. Especially in the cases of implants used for athletes engaged in contact sports [39] and for children [40], the implants may be removed after a healing period [34]. This necessitates the design of materials with a low Young's modulus and high mechanical strength, as well as low bone conductance for removable implant applications [31,34,41]. Problems that arise during implant removal surgery due to the assimilation of the bone and the implant material can be prevented by inhibition of calcium phosphate precipitations on the surfaces of the implant materials [34].

It is possible to prevent bone atrophy during the time that the implant stays in the body by using implant materials with a low Young's modulus [42]. By minimizing or eliminating the stress shielding effect with the use of implant materials that have a low Young's modulus, problems relating to long recovery times of patients following removal operations [39] can be resolved.

The objective of this study was to develop Ti alloys with low rigidity, high mechanical strength, and reasonable elongation at rupture for removable bone tissue implant applications. To this end, studies showing that zirconium (Zr) prevents calcium phosphate formation on the surface of a material [27,43,44] and studies describing the mechanical properties and phase stability changes of Ti–Nb–Zr alloys containing high amounts of Zr [45,46] were taken into account, and TNZ alloys with high Zr element (between 25 wt.% and 40.7 wt.%) were manufactured. Niobium (Nb), another of the alloy elements used in this study, is a β isomorphous alloy element [47]. Whereas the effect of Zr on binary Ti alloys is evaluated as either neutral or weak β stabilization, Zr functions as an effective β stabilizer in multi-element Ti alloys that contain Nb or Ta [48]. In this study, the effects of Zr and Nb content on the microstructures, mechanical properties, and cytocompatibility of TNZ alloys with different electronic parameters were investigated and compared.

2. Materials and methods

2.1. Alloy design

Using a trial-and-error method for the design of Ti alloys results in time-consuming and uneconomical manufacturing processes [49]. The approach developed by Morinaga et al. [50], known as the d-electron alloy design method, exploits the relationship between the phase stability and elastic properties of Ti alloys by using the electronic parameters of average bond order ($\overline{B_o}$) and average metal d-orbital energy level ($\overline{M_d}$) [48]. In the literature, there are reports of many Ti alloys that have been designed using the d-electron alloy design method [11,51–53]. It was reported by Abdel et al. [48] that Young's modulus decreases along the β/β + ω phase boundary with an increase in $\overline{B_o}$ and $\overline{M_d}$ values, as seen in the $\overline{B_o} - \overline{M_d}$ diagram (Fig. 1) (adapted and redrawn from Ref. [48], Copyright (2006), with permission from Elsevier). β/β + ω phase boundary presented with a dotted curve in Fig. 1, means that, the phase stability of titanium alloys depends on the amount of other alloying elements (e.g. Hf, Zr), as explained in Ref. [45].

B_o is the measure of the covalent bond strength between Ti and the alloying element, whereas the M_d of the alloying transition-metal is a value that relates the metallic radius of the elements and their electronegativities [48]; these two parameters are values that have been theoretically determined using the orbital method in body-centered cubic titanium using the DV-Xα molecular orbital method [48,50]. The average $\overline{B_o}$ and $\overline{M_d}$ values are calculated using the formula given by [54]:

$$\overline{B}_o = \Sigma X_i (B_o)_i \tag{1}$$

$$\overline{M}_d = \Sigma X_i (M_d)_i \tag{2}$$

where X_i is the atomic ratio of the given element, $(B_o)_i$ is the bond order value of the given element [54], and $(M_d)_i$ is the metal