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Use of first principles and Thermo-Calc to identify potential low elastic modulus titanium-based alloys for biomedical applications

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Abstract

High alloyed β-phase stabilised titanium alloys are known to have low elastic moduli comparable to that of the human bone (≈30 GPa). The β-phase in titanium alloys exhibits an elastic modulus of about 60-80 GPa, which is nearly half that of α-phase (100-120 GPa). In this work, an attempt to develop a β-phase titanium-based alloy through first-principles calculations and Thermo-Calc calculations for biomedical applications was conducted. First-principles calculations were performed using the CASTEP code on a simple 2-atom bcc unit cell to predict the theoretical elastic modulus and mechanical stability of the Ti-Nb-Ta-Zr (TNTZ) system at 0 K. Thermo-Calc was used to determine the phase proportion diagrams of the proposed alloys at 500°C. The alloy comprised Ti-Nb_x-Ta_{25}-Zr_5 (x = 5, 10, 20, 30, 40) (at.%). The theoretical results suggested that increasing niobium content introduced both mechanical ($c' > 0$) stability of the alloys. Alloy Ti-Nb_5-Ta_{25}-Zr_5 gave the lowest elastic modulus of 55.23 ± 24.45 GPa which is half the elastic modulus of pure titanium (α phase). The phase proportion diagrams showed that up to 58.6 mol.% of β phase was retained at 20 at.% Nb, although the Voigt-Reuss-Hill Young's modulus calculated from first principles increased with increasing niobium content while the α/β phase transformation temperature decreased down to 551.3°C at 40 at.% Nb.

Keywords: Titanium alloys, Elastic modulus, First principles, Thermo-Calc

1. Introduction

Metallic implants such as stainless steel, cobalt-chromium based alloys and titanium and its alloys are preferred biomaterials, especially in areas requiring superior mechanical strength (Mohammed, Khan, & Siddiquee, 2014). Amongst the currently used metallic biomaterials, titanium-based alloys are extensively used due to their excellent biocompatibility, corrosion resistance, wear resistance, high specific strength, as well as low modulus of elasticity relative to other conventional metallic biomaterials (Kuroda & et al., 1998; Niinomi, 2008). Amongst all these excellent properties of titanium alloys, the modulus of elasticity is one of the key drivers for developing these alloys for biomedical applications. High elastic modulus puts serious limitations on the performance of titanium alloys as implants, especially for artificial joints e.g. knee, shoulder, hip. An implant with higher stiffness relative to that of the adjacent bone results in bone resorption (Niinomi, Liu, Nakai, Liu, & Li, 2016) and cell death around the implant and consequently osteoporosis or implant loosening (Gaaser, 2001). This biomechanical incompatibility is called the "stress shielding effect" (Sumnar, Turner, Igloria, Urban, & Galante, 1998). It is therefore essential that the elastic modulus or stiffness of the implant is as close to that of the connected bone as possible, to facilitate effective transfer of mechanical stress needed by the bone (Sumner & Galante, 1992; Mohammed, Khan, & Siddiquee, 2014). Commercially pure (CP) titanium and the Ti-6Al-4V alloy (ASTM F1108) are currently the most commonly used materials as structural biomaterials for orthopaedic prosthesis and dental implants (Niinomi, Fatigue performance and cyto-toxicity of low rigidity titanium alloy, Ti-29Nb-13Ta-4.6Zr, 2003; Geetha & et al., 2009) (Geetha & et al., 2009; Niinomi, 2003). However, Al and V in Ti-6Al-4V are associated with long-term health problems such Alzheimer's, neuropathy and ostemomalacia (Nag, Banerjee, & Fraser, 2005). Vanadium is toxic, both in elemental and oxide (V_2O_5) form, and it alters the kinetic activity of enzymes in the body tissues. This phenomenon is associated with inflammatory response of the cells (Okazaki, Ito, Kyo, & Tateishi, 1996). The release of aluminium ions into the tissues potentially causes Alzheimer's disease (Ikeda, Komatsu, Sowa, & Niinomi, 2002). As well as the toxicity of the alloying elements, the biomechanical incompatibility (i.e. high elastic or Young's modulus) of commercially (CP) titanium (~100 GPa) and Ti-6Al-4V (~110-112 GPa) (Long & Rack, 1998) implants relative to that of the human bone (10-30 GPa) (Miura, Yamada, Hanada, Jung, & Itoi, 2011) is problematic. The αTi phase in CP titanium and Ti-6Al-4V alloy promotes the high elastic modulus of the materials (Gross & Abel, 2001; Geetha & et al., 2009).

Recent trends in research and development of biomedical titanium alloys include low elastic modulus titanium-based alloys, also referred to as second generation biomaterials or beta (β) type titanium alloys, Table 1. These alloys must contain non-toxic and

Table 1: Titanium-based alloys and their respective mechanical properties for biomedical applications (Geetha & et al., 2009)

Material	Standard	Modulus (GPa)	Tensile strength (MPa)	Alloy type
1st generation biomaterials (1950-1990)				
CP Ti (grade 1-4)	ASTM 1341	100	240-550	α
Ti-6Al-4V ELI	ASTM F136, F1472	110-112	860-930	α + β
Ti-6Al-7Nb	ASTM F1295	110	900-1050	α + β
Ti-5Al-2.5Fe	-	110	1020	α + β
2nd generation biomaterials (1990-to date)				
Ti-13Nb-13Zr	ASTM F1713	79-84	973-1037	Metastable β
Ti-12Mo-6Zr-2Fe	ASTM F1813	74-85	1060-1100	β
Ti-35Nb-7Zr-5Ta	-	55	596	β
Ti-29Nb-13Ta-4.6Zr	-	65	911	β
Ti-35Nb-5Ta-7Zr-0.4O	-	66	1010	β
Ti-15Mo-5Zr-3Al	-	82	-	β
Ti-Mo	ASTM F2066	-	-	β

non-allergic elements and must possess excellent biomechanical properties (Li, Hao, Yang, Cui, & Niinomi, 2002; Li, et al., 2014; Wang, et al., 2016). Generally, elastic modulus decreases with increased volume fraction of the β phase. The elements that are known to enhance the volume fraction of β phase in titanium alloys by stabilising the β phase are Nb, Ta, Mo, Zr, Cr and V (Niinomi, 2002; Ikehata, et al., 2004; Abdel-Hady, Hinoshitaa, & Morinagaa, 2006; Karre, Niranjan, & Dey, 2015).

Niobium and tantalum are typically considered the most potent β stabilisers and effectively reduce the elastic modulus (Yang, et al., 2018). Zirconium is considered a neutral element and weak β stabiliser in the Ti-Zr alloy system (Correa, et al., 2015). However, in the Ti-Zr-Nb system, zirconium acts as a potent β stabiliser (Brailovsky, et al., 2011). Kim et al. (2020) studied Ti-Nb-Zr (Nb = 12-40, Zr = 0-18) (at.%), finding that the minimum Nb content to maintain the β phase at room temperature continuously decreased with increasing Zr content. Wang et al. (Wang, et al., 2018) studied the Ti-Zr alloy in the composition range of 5 to 45 wt% Zr and that only α and α′ phases existed in the entire composition range. Niobium and tantalum are more expensive and denser than pure titanium, so addition of large amounts of these metals is not economically viable and would also lead to considerable increase in the density of the β-type titanium alloys (Yang, et al., 2018). Thus, this work focused on developing compatible Ti-Nb-Ta-Zr alloys for biomedical applications by computational calculations, i.e. first principles calculations and Thermo-Calc calculations. The computational approach would reduce experimental effort, because they would identify good starting compositions, and hence reduce experimental time and consumption of the expensive metal powders (Nb, Ta and Zr). The alloys compositions comprised Ti-Nb_x-Ta_{25}-Zr_5 (x = 5, 10, 20, 30, 40) (at.%).

2. Computational methodology

2.1 First principles calculations

First principles calculations for the proposed β-type alloy Ti-Nb_x-Ta_{25}-Zr_5 (x = 5, 10, 20, 30, 40) (at.%) were conducted using density functional theory (DFT) within the generalised gradient approximation (GGA) (Burke, Perdew, & Wang, 1998) implemented in the Cambridge Serial Total-Energy Package (CASTEP) code (Clark, et al., 2005). The cut-off energy convergence used was 669.4 eV for the plane-wave basis, and the structural relaxation the Brillouin Zone (BZ) was sampled with a Monkhorst-Pack k-point grid (Monkhorst & Pack, 1976) of $(18/n_1) \times (18/n_2) \times (18/n_3)$ for the $n_1 \times n_2 \times n_3$ bcc βTi unit cell (where n_1, n_2 and n_3 are the numbers of the unit cells taken in the x, y and z-directions, and equated to 1 for all the calculations). The lattice constants were optimised using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) (Fischer & Almlof, 1992) minimisation algorithm at zero pressure from first-principles. The calculations were done at 0 K and the atoms were kept fixed at their lattice positions. The polycrystalline elastic properties were estimated as a function of composition based on the Voigt-Reuss-Hill approach. Voigt gives the upper elastic bound due to the assumption of constant strain in all grains, Reuss gives the lower bound due to the assumption of constant stress in all grains, and the Hill approach is the average of Voigt and Reuss which gives the closest figure to the polycrystalline value (Chung & Buessem, 1967). All the calculations were run at a maximum number of iterations of 100.

2.2 Thermo-Calc

The thermodynamic equilibrium of a system at constant pressure is given by the minimum of the Gibbs free energy, ΔG_f^o. For multiphase equilibria, the sum of the molar Gibbs energies for the stable phases is at minimum when $\Delta G_f^o = \sum_{\emptyset} n^{\emptyset} G_m^{\emptyset}$ (Kattner, 2016), where $n^{\emptyset}$ is the number of moles and $G_m^{\emptyset}$ is the molar Gibbs energy of phase Ø. Thermo-Calc is used to evaluate Gibbs energy parameters as a function of individual phases (Sundman, Jansson, & Andersson, 1985; Prins, Cornish, Stumpf, & Sundman, 2003; Liu, 2009). The database of the parameterised Gibbs energy function is usually built from the pure elements, and phases in binary and ternary alloys, and can be used to extrapolate thermodynamic properties of phases in alloys as a function of composition, temperature or pressure. In this work, the Gibbs energy functions of pure Ti, Nb, Ta and Zr for the Ti-Nb_x-Ta_{25}-Zr_5 (x = 5, 10, 20, 30, 40) (at.%) alloys were taken from the SS0L4 database in the Thermo-

Calc 2020a version. Single point equilibrium (SPE) calculations were performed to show stable phases and their compositions at 500°C and a pressure of 100 kPa. Calculations were also performed between 100°C and 2000°C to plot the proportions of phases as a function temperature.

3. Results and discussion

3.1 First principles calculations

Table 2 shows elasticity results of various alloys. For mechanically stable crystals, the independent elastic constants should satisfy the well-known Born stability criteria (Born, 1940), which for cubic structures is $c_{11} > 0$, $c_{44} > 0$, $c_{11} > |c_{12}|$ and $c_{11} + 2c_{12} > 0$.

In Table 2, the estimated elastic constants satisfied the Born stability criteria (Born, 1940). In addition, the increasing shear modulus, c', indicated that the alloys became more stable as the niobium concentration increased, Figure 1. The Cauchy pressure, c'', is used to ascertain the kind of bonds for metals and compounds (Pettifor, 1992). Brik (2010) observed that c'' is positive for most ionic bonds (e.g. metallic) and negative for most covalent bonds (non-metallic). Increasing values of Cauchy pressure relative to the Nb content confirmed that the metallic behavior of Ti-Nb_x-Ta_{25}-Zr_5 alloys became stronger with increasing Nb. The Zener anisotropy factor, A, is an indication of the degree of anisotropy in solids (Zener, 1948). For $A = 1$, the material is completely isotropic, whereas deviations from unity indicate the degree of elastic anisotropy which is defined as (Chung & Buessem, 1967):

$$A^* = {[3(A-1)^2]}\Big/{[3(A-1)^2 + 25A]}$$

Elastic anisotropy is the directional dependence of mechanical properties of a material, such as formation of micro-cracks, movement of cracks, development of plastic deformation (Naher & Naqib, 2021). A^* has the following properties of practical importance:

(a) A^* is zero for the crystals of elastic isotropy, i.e. for $A = 1$, (b) for an anisotropic crystal A^* is a single-valued measure of the elastic anisotropy regardless of whether $A < 1$ or $A > 1$ and (c) A^* gives a relative magnitude of the actual elastic anisotropy possessed by a crystal (Chung & Buessem, 1967).

The bcc crystal structure of alloys Ti-Nb_5-Ta_{25}-Zr_5, Ti-Nb_{10}-Ta_{25}-Zr_5 and Ti-Nb_{20}-Ta_{25}-Zr_5 was more elastically anisotropic than alloys Ti-Nb_{30}-Ta_{25}-Zr_5 and Ti-Nb_{40}-Ta_{25}-Zr_5.

Figure 1 also shows the lattice parameter (a) and shear modulus (c') of the bcc phase as a function of Nb content. The lattice parameter increased with increasing Nb concentration, which is due to the relative atomic sizes of Ti (176 pm) and Nb (198 pm) (WolframResearch, 2021). The atomic size of niobium is larger than that of titanium, hence an increase in the lattice parameter as Nb content increased

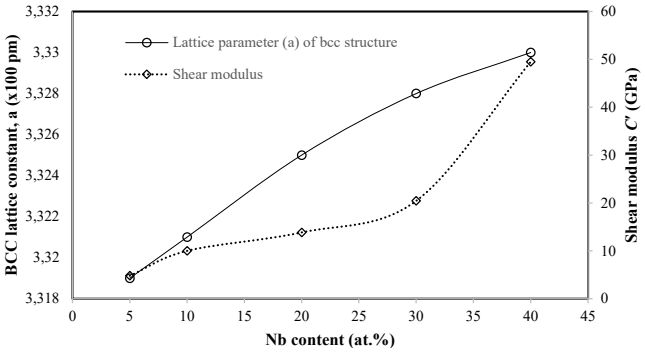


Figure 1: Effect of niobium content on lattice parameter and shear modulus Ti-Nb_x-Ta_{25}-Zr_5 alloys at 0 K

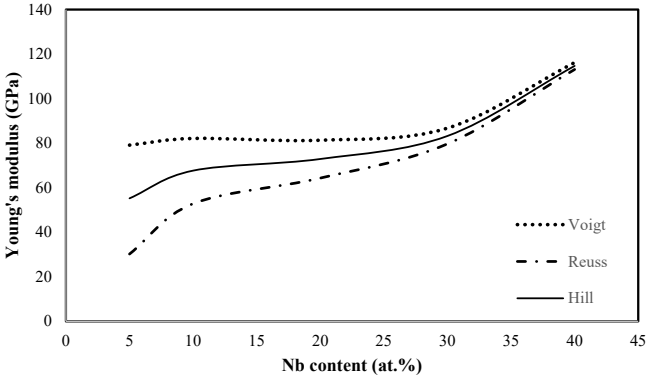


Figure 2: Effect of niobium content on Young's modulus of Ti-Nb_x-Ta_{25}-Zr_5 (x = 5, 10, 20, 30, 40 (at.%) at 0 K

Figure 2 shows the change in Young's modulus with Nb content, using the Voigt-Reuss-Hill (VRH) approximation. Young's modulus is defined as the ratio of uniaxial stress and axial strain, and is a measurement of the stiffness (Pugh, 1954) (larger Young's moduli indicate stiffer materials). The VRH approximation can provide satisfactory estimations of elastic moduli. The lowest averaged Young's modulus (Hill) obtained was 55.23 ± 24.5 GPa for the Ti-Nb_5-Ta_{25}-Zr_5 alloy, although this had large scatter.

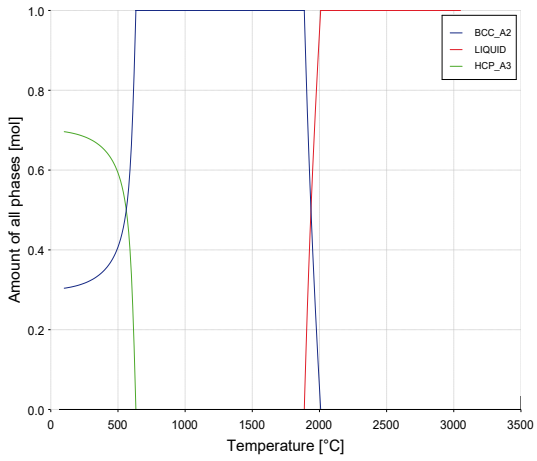
3.2 Thermo-Calc calculations

Figure 3 shows the phase proportion diagrams of the alloys as a function of temperature. Increased Nb content gradually reduced the start of β → α transformation temperature from 882°C for CP titanium to 551.3°C for 40 at.% Nb. Alloys Ti-Nb_{30}-Ta_{25}-Zr_5 and Ti-

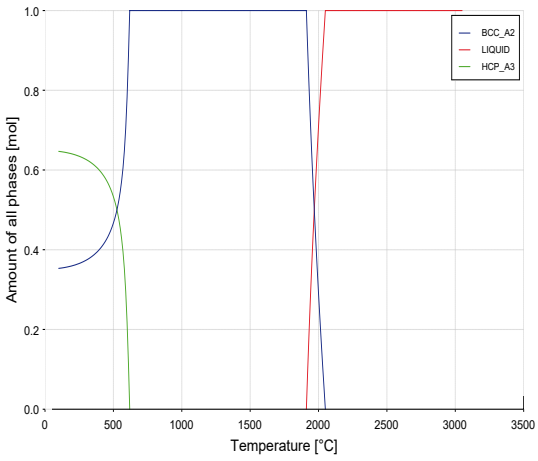
Table 2: Elastic properties of Ti-Nb_x-Ta_{25}-Zr_5 alloys at 0 K

Nb (at.%)	c_{11}	c_{44}	c_{12}	c'	c''	A	A^*
5	133.4	44.02	123.8	4.80	79.78	9.171	0.466
10	143.8	42.40	123.8	10.0	81.40	4.24	0.229
20	155.3	39.14	127.6	13.85	88.46	2.826	0.124
30	170.5	38.02	129.6	20.45	91.58	1.859	0.0455
40	311.7	35.13	212.7	49.5	177.6	0.7097	0.0140

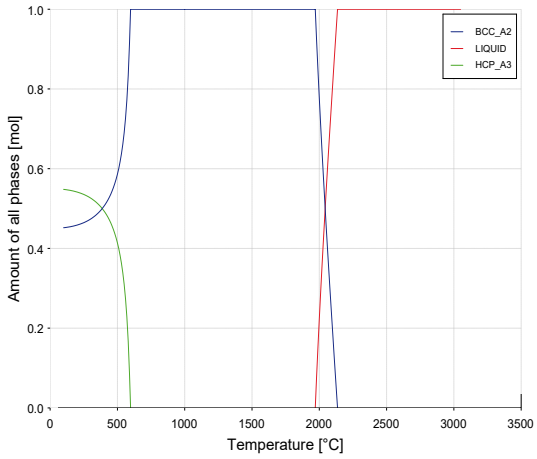
* $c' = ½(c_{11} - c_{12})$, $c'' = c_{12} - c_{44}$, $A = 2c_{44}/(c_{11} - c_{12})$



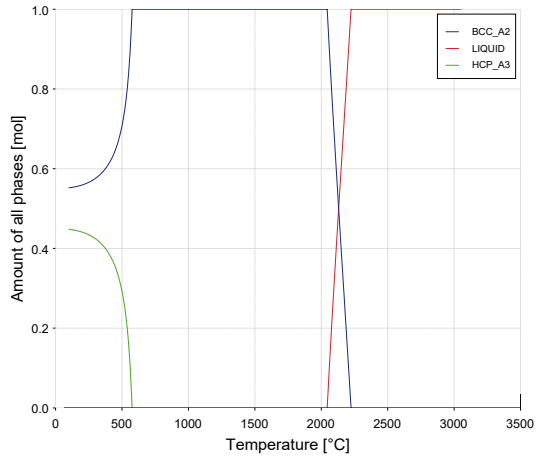
$Ti\text{-}Nb_5\text{-}Ta_{25}\text{-}Zr_5$



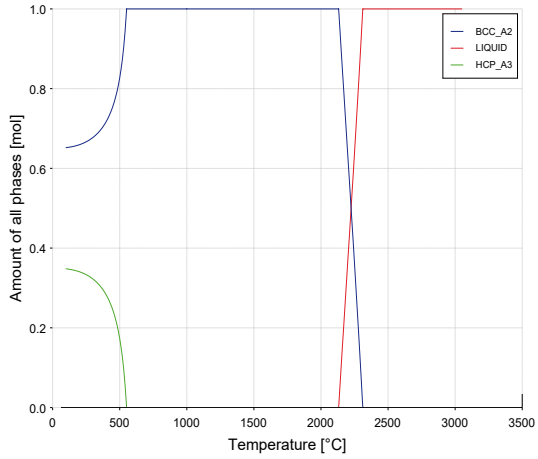
$Ti\text{-}Nb_{10}\text{-}Ta_{25}\text{-}Zr_5$



$Ti\text{-}Nb_{20}\text{-}Ta_{25}\text{-}Zr_5$



$Ti\text{-}Nb_{30}\text{-}Ta_{25}\text{-}Zr_5$



$Ti\text{-}Nb_{40}\text{-}Ta_{25}\text{-}Zr_5$

Figure 3: Calculated phase proportion diagrams of $Ti\text{-}Nb_x\text{-}Ta_{25}\text{-}Zr_5$ (x = 5, 10, 20, 30, 40 at.%)

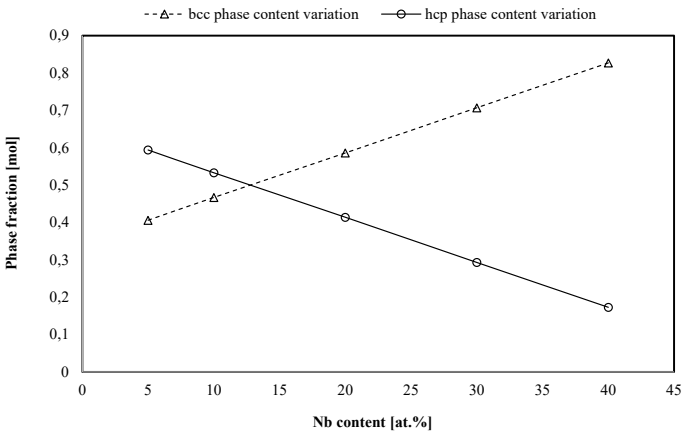


Figure 4: Phase proportions of α (hcp) and β (bcc) as a function of niobium content at 500°C

Nb_{40}-Ta_{25}-Zr_5 were favourable, since more β phase was stabilised compared to other alloys. This can be attributed to the higher Nb content as a stronger β stabiliser (Yang, et al., 2018).

Figure 4 shows the variation in phase proportion with Nb content. The data were generated from single point equilibrium (SPE) calculations and only two equilibrium phases (α and β) were observed. The amount of β (bcc) phase increased with increasing Nb content, thus confirming the potency of Nb as a β stabiliser. At 20 at.% Nb, the amount of equilibrium β phase was 58.6 mol.% at 500°C, i.e. more than the α phase. The experimental results of Okazi et al. (2004), Kim et al. (2006) and Gutierrize et al. (2014) showed that the β phase was the major phase in alloys with higher than 25 at.% Nb.

The increasing β content with increasing Nb content (Figures 3 and 4) is, however, not in agreement with the predicted elastic Young's modulus from first principles calculations (Figure 2). As noted by Niinomi (2008), increasing β phase content contributes significantly to the reduction of the elastic Young's modulus. However, the first principles results (Figure 2) agreed well with Wang et al. (2016).

In summary, first principles calculations showed Ti-Nb_5-Ta_{25}-Zr_5 as the potential alloy due to its lower elastic Young's modulus with a positive shear modulus. In addition, the calculations from Thermo-Calc showed that over 50 mol.% of β phase can be achieved at a minimum Nb content of 20 at.% The phase stability analysis for the alloys will be done in future studies through the application of Pandat software package.

4. Conclusions

a. First principles density functional theory (DFT) within generalized gradient approximation (GGA) was conducted at 0 K to determine the elastic properties (Young's modulus, shear modulus, Cauchy pressure, elastic anisotropy and the bcc lattice constant) of alloys Ti-Nb_x-Ta_{25}-Zr_5 (x = 5, 10, 20, 30, 40) at.% in a CASTEP code.

b. Increased Nb content to 40 at.% improved the mechanical stability and isotropy of the alloys.

c. Increased Nb content to 40 at.% increased the lattice parameter while the alloys remained mechanically stable, shown by the calculated shear moduli ($c' > 0$).

d. The Voigt-Reuss-Hill approximation showed that the Young's modulus increased with Nb content to 40 at.%. Alloy Ti-Nb_5-Ta_{25}-Zr_5 had the lowest Young's modulus of 55.3 ± 24.45 GPa (although this had large scatter) and this value is closest to the cortical Young's modulus of the human bone.

e. Thermo-Calc calculations were used to investigate the equilibrium phase proportions of the proposed alloys using SS0L4 database.

f. Thermo-Calc showed that the β phase became more stable with increased Nb content.

g. Up to 58.6 mol% of β phase was achieved at 20 at.% Nb at 500°C. The transformation temperatures decreased as the Nb content was increased, with alloy Ti-Nb_{40}-Ta_{25}-Zr_5 reaching the lowest phase transformation temperature of 551.3°C.

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Contribution of each author

M N Madigoe: Conceptualisation, Design of the work, Data acquisition, analysis and interpretation, writing and editing of the manuscript. **R Modiba:** First principles calculations and interpretation, Critical revising and editing of the manuscript. **L A Cornish:** Data interpretation (first principles and Thermo-Calc calculations), Critical reviewing and editing of the manuscript, Final approval of the manuscript.

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