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Effects of alloying elements on the elastic properties of bcc Ti-X alloys from first-principles calculations

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ABSTRACT

Titanium alloys are great implant materials due to their mechanical properties and biocompatibility. However, a large difference in Young's modulus between bone (~10–40 GPa) and common implant materials (ie. Ti-6Al-4V alloy ~110 GPa) leads to stress shielding and possible implant failure. The present work predicts the single crystal elastic stiffness coefficients (c_{ij}'s) for five binary systems with the body centered cubic lattice of Ti-X (X = Mo, Nb, Ta, Zr, Sn) using first-principles calculations based on Density Functional Theory. In addition, the polycrystalline aggregate properties of bulk modulus, shear modulus, Young's modulus, and Poisson ratio are calculated. It is shown that the lower Young's modulus of these Ti-alloys stems from the unstable bcc Ti with a negative value of (c_{11}–c_{12}). The data gathered from these efforts are compared with available experimental and other first-principles results in the literature, which set a foundation to design biocompatible Ti alloys for desired elastic properties.

1. Introduction

Titanium (Ti) and its alloys have been used in biomedical applications for many years due to their biocompatibility and corrosion resistance [1]. In recent years, there has been an increasing interest in finding better materials for the load-bearing implants due to the increase in total knee and hip arthroplasties. Krutz et al. [2] predicted that the total number of hip replacements and knee arthroplasties would grow by 174% and 673% from 2005 to 2030, leading to 572,000 hip replacements and 3.48 million knee procedures in 2030, respectively. Not only is the total number of procedures increasing but there is also a rise in the younger aged population needing knee and hip replacements [3]. The younger age calls for more revision surgeries due to the fact that total hip and knee replacements only last 7–12 years at the best. The primary considerations for better biomedical implants, such as load-bearing knee and hip implants, are to find biocompatible materials that have fatigue limits comparable to that of Ti-6Al-4V at 10^7 cycles (90–610 MPa depending on the manufacturing conditions), and a Young's modulus closely matching that of bone (10–40 GPa) [1].

The common alloys used for these applications are Ti-6Al-4V, stainless steels, and MoCoCr alloys [4,5]. In recent years, aluminum and vanadium have been observed to cause cytotoxicity [6]. Another issue with the common implant materials is stress shielding, which leads to implant failure. Stress shielding occurs when the Young's modulus of the implant is higher than that of bone. Due to the elastic difference, load application to the joint results in the implant material absorbing all of the stress and causing the bone surrounding the implant to atrophy, which leads to a loss in bone density, implant loosening and failure [1]. Table 1 summarizes the Young's moduli of the common implant materials (>100 GPa) compared to that of bone (10–40 GPa) [1]. It is shown that these implant materials have a large elasticity mismatch with bone.

Ti is stable in the hexagonal close packed (hcp, α) structure under ambient temperature and pressure. However, body centered cubic (bcc, β) Ti alloys have received much attention due to their low Young's modulus and high specific strength, in conjunction with the fact that the bcc phase can be stabilized by many non-toxic elements that show excellent corrosion resistance and no allergy problems [7]. The elements such as Mo, Nb and Ta are all biocompatible elements and strong β-stabilizers, while Zr is a biocompatible weak β-stabilizer by itself but a strong stabilizer when in combination with other elements [8]. Recently, Tin (Sn) has also been studied for use in Ti-alloys due to the low cost and the fact that in small concentrations does not affect the Ti-alloys biocompatibility [5]. Thus far, various Ti alloys have been experimentally studied, such as Ti-13Nb-13Zr (wt.% for alloying elements unless otherwise stated hereafter), Ti-35Nb-5Ta-7Zr-0.4O, Ti-29Nb-Ta-Zr

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Table 1
Young's modulus of common implant materials compared with the Young's modulus of bone [1].

Alloy	Young's modulus (GPa)
Bone	10–40
cp-Ti*	105
Ti-6Al-4V	110
Stainless Steel	200
CoCrMo	200–230

* cp-commercially pure titanium.

and Ti-25Nb-Ta-Zr and have a Young's moduli between 71 and 57 GPa [1,7,9], which is starting to approach the Young's modulus of bone. While new metallic alloys are continuously being developed, it is necessary to determine the effects of alloying elements on the elastic properties as well as the stable region of bcc Ti-X alloys to guide the alloy design.

The present work is a systematic study of the single crystal elastic stiffness coefficients (c_{ij}'s) and polycrystalline aggregate properties of bcc Ti-X (X = Mo, Nb, Ta, Sn, Zr) alloys. The elastic properties were calculated using first-principles calculations based on Density Functional Theory (DFT). The composition dependence of elastic properties of Ti-X alloys is explored through dilute solutions and special quasirandom structures (SQS) [10] for concentrated solutions using the methodologies outlined in Section 2. The obtained elastic properties and potential applications are presented and discussed in Section 3, and conclusions are given in Section 4.

2. Computational methodology

2.1. Single crystal bcc elastic properties

In order to obtain the equilibrium properties and the ground state energy at 0 K without the contribution of zero-point vibrational energy, an equation of states (EOS) fitting was carried out with 5 or more different volumes of the same composition using a four-parameter Birch-Murnaghan (BM4) EOS as suggested by Shang et al. [11]:

$$E_0(V) = a + bV^{-2/3} + cV^{-4/3} + dV^{-2} \tag{1}$$

where a, b, c and d are fitting parameters. From this EOS fitting, the bulk modulus (B_0), energy (E_0), volume (V_0) and the derivative of bulk modulus with respect to pressure (B_0') can be calculated for each structure at equilibrium.

The single crystal elastic stiffness coefficients c_{ij}'s were calculated from the ground state energy structure using a stress–strain method developed by Shang et al. [12]. With this method, a set of independent strains $\varepsilon = (\varepsilon_1, \varepsilon_2, \varepsilon_3, \varepsilon_4, \varepsilon_5, \varepsilon_6)$ were imposed on the crystal lattice, where ε_1, ε_2, and ε_3 are the normal strains, ε_4, ε_5, and ε_6 the shear strains, and a set of stresses $\sigma = (\sigma_1, \sigma_2, \sigma_3, \sigma_4, \sigma_5, \sigma_6)$ were generated. Hooke's law was used to calculate the elastic stiffness coefficients:

$$\begin{pmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ c_{12} & c_{22} & c_{23} & 0 & 0 & 0 \\ c_{13} & c_{23} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{66} \end{pmatrix} = \begin{pmatrix} \varepsilon_{1,1} & & \varepsilon_{1,n} \\ \varepsilon_{2,1} & & \varepsilon_{2,n} \\ \varepsilon_{3,1} & \cdots & \varepsilon_{3,n} \\ \varepsilon_{4,1} & & \varepsilon_{4,n} \\ \varepsilon_{5,1} & & \varepsilon_{5,n} \\ \varepsilon_{6,1} & & \varepsilon_{6,n} \end{pmatrix}^{-1} \begin{pmatrix} \sigma_{1,1} & & \sigma_{1,n} \\ \sigma_{2,1} & & \sigma_{2,n} \\ \sigma_{3,1} & \cdots & \sigma_{3,n} \\ \sigma_{4,1} & & \sigma_{4,n} \\ \sigma_{5,1} & & \sigma_{5,n} \\ \sigma_{6,1} & & \sigma_{6,n} \end{pmatrix} \tag{2}$$

where "−1" represents the pseudo-inverse.

To model the elastic properties as a function of composition, the Redlich-Kister [13] polynomial, commonly used in the CALPHAD modeling approach [14] to model the Gibbs energy equations, was adapted according to previous work to model the elastic properties by introducing binary interaction parameters (L_0 and L_1) for each Ti-X binary alloy [14,15]:

$$c_{ij}(x) = \sum [x_A c_{ijA} + x_B c_{ijB} + L_0 x_A x_B + L_1 x_A x_B (x_A - x_B)] \tag{3}$$

where x_A and x_B, are the mole fraction of elements A and B respectively, and c_{ijA} and c_{ijB} are the elastic stiffness coefficients of pure bcc elements A and B. When calculating the elastic stiffness coefficients of multi-component alloys, the interaction parameters for each binary alloy contained in the multi-component alloy are summed as shown in Eq. (3). The interaction parameters were evaluated using the values from the first-principles calculations. With the focus being Ti-rich alloys, the first-principles results with 70 at.% Ti or higher were weighted heavier (×6, according to the authors' practices) than the other points for the parameter evaluation. The amount of weighting was adjusted until the proper weighting was found. This was determined because up to ×6, the weighting improved the predictions on the Ti-rich side. Any weighting higher than ×6 had little to no effect on the predicted results on the Ti-rich side.

2.2. Computational details

In the present work, the Vienna ab initio Simulation Package (VASP) [16] was employed to calculate the elastic properties of the pure elements and Ti-containing binary systems in the bcc phase. The ion–electron interactions were described using the projector augmented wave (PAW) [17,18] method. Two different exchange–correlation (X-C) functionals, the generalized gradient approximation (GGA) implemented by Perdew and Wang (PW91) [19] and the Perdew, Burke, and Ernzerhof (PBE) [19], were tested on a single binary system along with seven magnitudes of strain, 0, ±0.01, ±0.013 and ±0.007. Both the X-C functionals and the magnitudes of strain showed little variance in results, thus the calculations were done with PBE and ±0.01 strains. For consistency, a 310 eV energy cutoff was adopted for all calculations, which is roughly 1.3 times higher than the default value. The Methfessel-Paxton method (ismear = 1) was used to get the accurate atomic positions, while for the final calculations we chose the tetrahedron method with Blöchl corrections (ismear = −5) to get accurate total energy and stresses (not forces acting on atoms, which cannot be accurately calculated by ismear = −5 for metals). The smearing widths are the default ones for ismear = 1 (and −5). Note that it is not sensitive for the method of ismear = −5. The convergence tolerances used for the electronic self-consistency cycles was 1E−6 and the structural relaxations was 1E−5. The energy convergence criterion was 10^{-6} eV/atom, and the Monkhorst-Pack scheme was used for Brillouin zone sampling [16,20]. The valence configuration for each element is listed in Table 2 with pv, sv, and d referring to the p, s, or d states that were treated as valence, respectively, based on the VASP suggestions [16,17].

For the Ti-X binary systems, calculations for both dilute and SQS solutions [10] were carried out. At most five dilute solutions were calculated for the Ti-X binary alloy using supercell sizes, i.e., $Ti_{53}X$ (54-atom), $Ti_{15}X$ (16-atom), Ti_7X (8-atom), $X_{15}Ti$ (16-atom), and $X_{53}Ti$ (54-atom).

Three 16-atom SQS cells with mole fractions of X atoms at 0.25, 0.5, 0.75 were employed. SQS are small supercells used to mimic randomly substituted structures in terms of a correlation function while miminizing the error of calculating actual random structures with DFT. The size of the bcc SQS supercells was extensively