First Principles Estimation of Bulk Modulus and Theoretical Strength of Titanium Alloys

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Titanium alloys are favorable implant materials for medical applications, due to their desirable mechanical properties and biochemical compatibility. However, current bio-titanium alloys were formulated principally by trial and error, which by no means represents the optimum. Here a theoretical investigation of the influence of alloying elements and interstitial elements on the bulk modulus and theoretical strength of \(\alpha\)-titanium was presented. The bulk modulus and theoretical strength were estimated from the binding energy against the unit cell volume curves calculated by means of first principles discrete variational cluster method. The results of the calculation suggested that the 3d elements Cr, Mn, Fe, and Co, as well as all the interstitial elements considered in this study (H, B, C, N and O), are capable of enhancing the relative admissible strain of \(\alpha\)-titanium.

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1. Introduction

Titanium-based alloys are widely used as load-bearing orthopaedic implants, due to their relatively good fatigue resistance and biological passivity. One of the examples is the application of Ti–6Al–4V as femoral stems in total hip replacements. However, these materials still suffer from a large degree of biomechanical incompatibility, due to their relatively high elastic modulus (about 120 GPa), compared with that of the bone (max. 30 GPa). When used as hip implants, e.g. a femoral stem, titanium overtakes a considerable part of the body loading, which shields the bone from the necessary ‘stressing’ required to maintain its strength, density, and healthy structure. Such an effect, usually termed ‘stress shielding’, eventually causes bone loss, implant loosening, and premature failure of the artificial hip. Moreover, the existing alloys can also release toxic ions (e.g. V and Al) into the body, leading to undesirable long-term effects. These result in the current implant life being around 10–15 years in vivo, whereas a desirable implant should last as long as the patient’s life span, without causing any discomfort to the patient. Such an implant material has not been developed yet.

The ideal material should possess good strength, high fatigue resistance, and a low elastic modulus. Materials engineers have devoted considerable efforts to enhance the yield strength and to reduce the modulus. Some new \(\beta\)- and \((\alpha + \beta)\) titanium alloys have been developed for application as medical implants.\textsuperscript{1) However, all these compositions were formulated principally by trial and error, which by no means represents the optimum. It is desirable to understand the effects of alloying and structural variation on the essential mechanical properties of materials from theories in order to guide the design of new materials. Recently, Deyirmenjian et al. investigated the effects of atomic-scale voids on the strength and mechanical behaviour of defective systems using the \textit{ab initio} total energy pseudopotential method.\textsuperscript{2) There has been little theoretical investigation to guide alloy development for high strength, low modulus biomedical materials. The authors have carried out a preliminary study using the first principles theory to evaluate the modulus and the theoretical strength of pure metals\textsuperscript{3,4} and alloys.\textsuperscript{5,6} Kuroda \textit{et al.}\textsuperscript{7) have performed an investigation on some \(\beta\)-type titanium alloys composed of non-toxic elements Nb, Ta, Zr, Mo and Sn based on molecular orbital calculations of electronic structures. However, these reports are inconsistent regarding the effects of alloying elements on the level of reduction (or increase) in the modulus. Alloy of a given nominal constitution is shown to have different moduli after different processing histories. Although elastic modulus is sensitive to the fraction of constituent phases, it is not so sensitive to the way the different phases distribute in the alloy. For an alloy with fixed fractions of different phases, elastic modulus mainly depends on chemical composition. So in this study, we focus on the chemical influence on the elastic modulus of \(\alpha\)-titanium.

Transition metals are the most commonly used alloying additions in titanium alloys for biomedical applications. On the other hand, interstitial elements such as H, B, C, N and O, are usually unavoidable. In this paper, we report an investigation of the influence of alloying elements (Sc, V, Cr, Mn, Fe, Co, Ni and Cu) and interstitials (H, B, C, N and O) on the modulus and theoretical strength of \(\alpha\)-titanium. The electronic structure and the binding energy of the considered systems were calculated using the first principles discrete variational cluster method (DVM).\textsuperscript{8)

2. Method of Calculation

The discrete variational cluster method (DVM) was originally introduced by Ellis and co-workers,\textsuperscript{9) in which the total energy of a system, \(E_{\text{tot}}\), is expressed as a function of the electron density and the type and the arrangements of atomic nuclei:
where $\rho(\mathbf{r})$ is the electron density at a point $\mathbf{r}$ in real space, and the set $\{\mathbf{R}_A\}$ denote the positions of all atoms $A$ in the system under consideration.

The molecular electron density $\rho(\mathbf{r})$ can be evaluated from

$$\rho(\mathbf{r}) = \sum_i \sum_{l,k} f_i C_{il} \chi_i^*(\mathbf{r}) \chi_k(\mathbf{r})$$

where $f_i$ is the number of electrons occupying the $i$th molecular orbital $\phi_i$, which is expressed as a linear combination of atomic orbitals $\chi_i(\mathbf{r})$. $C_{il}$ is the coefficients of the atomic orbital $l$ in the molecular orbital $i$. $\mathbf{r}$ is the coordinates of the electrons. The star symbol in eq. (2) denotes the complex conjugation.

The total energy of a given system is defined as (in a.u.):

$$E_{\text{tot}} = \sum_i \varepsilon_i f_i - \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \int \rho(\mathbf{r}) [E_x(\mathbf{r}) - V_{xc}(\mathbf{r})] d\mathbf{r} + \frac{1}{2} \sum_{\lambda,\kappa} \frac{Z_{\lambda} Z_{\kappa}}{R_{\lambda,\kappa}}$$

where $\varepsilon_i$ is the energy of the molecular orbital $i$, $R_{\lambda,\kappa}$ is the distance between atoms $\lambda$ and $\kappa$, and $Z_i$ is the charge of an atomic nucleus. The second term on the right-hand side of the equation is the Coulomb interaction between electrons at positions $\mathbf{r}$ and $\mathbf{r}'$. The exchange-correlation energy $V_{xc}$ and potential $V_{ee}$ are represented by the Hedin-Lundqvist function for non-spin-polarized systems.

The binding energy $E_b^i$ of a system is estimated from the difference between the total energy of the system under consideration, $E_{\text{tot}}$, and the sum of energies of all the atoms constituting the system, $E_{\text{atom}}$, i.e.,

$$E_b^i = E_{\text{tot}} - \sum_i E_{\text{atom}}^i$$

The relationship between the binding energy and the volume of a unit cell is determined by the calculation of the binding energy as a function of the hydrostatic strain.

Theoretical strength is related to the maximum force that may be applied to a material without perturbing its stability. In order to determine the theoretical strength under hydrostatic tension, the electronic structure was calculated at $T = 0$ K. The internal pressure, $p$, was determined according to $p = -dE_{\text{tot}}/dV$ and the external stress $\sigma = -p$. The theoretical strength, $\sigma_{th}$, can be estimated by the relationship

$$\sigma_{th} = n \frac{dE_b(V)}{dV} \bigg|_{V = V_0}$$

where $E_b$ is the binding energy per atom ($E_b = E_b^i/N$, $N$ is the total number of atoms in a considered system), $V$ is the volume of a unit cell, $V_0$ is the volume of the unit cell at the inflexion point of the binding energy curve, and $n$ is the number of atoms in the unit cell. The bulk modulus, $B$, is determined as

$$B = nV \frac{d^2E_b(V)}{dV^2} \bigg|_{V = V_0}$$

where $V_0$ is the volume of the unit cell at the equilibrium point.

A representative cluster of 37 atoms was chosen here for the calculation of the electronic structure and the binding energy of selected Ti-X systems. The center Ti atom was replaced by an alloying atom in the case of binary titanium ‘alloys’, while the interstitial atom occupies an octahedral interstitial site in case of $\alpha$-titanium containing an interstitial atom, respectively. The Hamiltonian matrix elements and the overlap matrix elements were calculated with the Diophantus method, in which an integral was estimated approximately by a weighed sum over a set of sampling points. The radial part of the distribution function was chosen as a linear combination of the Fermi function located at each nucleus in the present paper. The total number of sampling points for the considered systems was 27000 in the calculation. A self-consistent charge approximation was introduced and the convergence criterion was that the difference between two consecutive values of the charge self-consistent integration was less than $10^{-4}$.

3. Numerical Results and Discussion

3.1 Binding energy

The variation in the binding energy as a function of the unit cell volume was calculated by varying the lattice parameter while keeping the hcp crystal structure of the matrix and keeping the ratio of $c$ to $a$ at its equilibrium value in the case of binary titanium ‘alloys’. For the system containing an interstitial, the curves were obtained through four different conditions. In the first case, the binding energies were evaluated after the determination of the energetically minimum state or the theoretical equilibrium state by compressing or stretching all the matrix titanium atoms to a relatively large strain. In the second case, the binding energies were calculated under the conditions where the first nearest neighbor atoms of the interstitial atom were compressed or stretched while other atoms in the cluster were fixed at their theoretical equilibrium positions (after relaxation), while the positions of other atoms are altered to determine the binding energy curves against the unit cell volume. In the fourth case, all of the above relaxations were carried out, and the binding energy curves were re-evaluated at the new configuration. Our previous work shows that, for transition metals, the interactions beyond the second nearest neighbor atoms do not seriously influence the accuracy of the binding energy calculation (the relative difference between the minimum binding energies obtained with the cluster including the second and the third nearest neighbor atoms is within 1.5%). So the accuracy of the present calculation should be even higher than the previous calculations.

The binding energy curves are plotted in Fig. 1. The alloying elements reduce the binding energy within 3%, except Sc, Ni, and Cu, which slightly increase the binding energy, implying that they are hard to dissolve into $\alpha$-Ti. The influence of interstitials on the binding energy is that they reduce the binding energy by less than 1.5%, except hydrogen, which causes an increase of the binding energy. This is in agreement with the fact that hydrogen is a stabilizer of the $\beta$ phase.
3.2 Influence of ‘extra’ elements on the bulk modulus and theoretical strength

The elastic behavior of titanium is nearly isotropic.\textsuperscript{12,13) The influence of the alloying elements and the interstitial atoms is shown in Fig. 2. To denote the difference between the small cluster under study and a real alloy, we regard the foreign atom in the cluster as ‘extra’ rather than ‘alloying’ in the conventional sense. To describe the effects of the ‘extra’ elements on the bulk modulus, the relative change in the theoretical bulk modulus, $\Delta B$, was plotted in Fig. 2, where

\[ \Delta B = B / B(Ti) \]

$B$ and $B(Ti)$ are the theoretical bulk moduli of $\alpha$-Ti with and without an ‘extra’ atom, respectively. The 3d transition elements Sc, Ni and Cu reduce the bulk modulus in the range of 2.5–6%, while Cr, Mn, Fe, and Co increase the bulk modulus in the range of 1–3.5%. In the case of Ti containing an interstitial atom, H and B reduce the bulk modulus, while C, N, and O increase it. From the viewpoint of reducing the modulus, H, B, Sc, Ni, and Cu are suitable, but they are energetically unfavorable as shown in Fig. 1. The influence of the ‘extra’ elements on the theoretical strength is shown in Fig. 3. Similar to the bulk modulus, the effect of ‘extra’ elements on the theoretical strength is described with the relative change in the strength of titanium with and without the ‘extra’ atom, $\Delta \sigma_{th}$, where $\Delta \sigma_{th} = \sigma_{th} / \sigma_{th}(Ti)$, and $\sigma_{th}$ and $\sigma_{th}(Ti)$ denote the theoretical strengths of titanium with and without the ‘extra’ atom, respectively. Cu and Ni dramatically reduce the theoretical strength, while Sc and V also have a negative effect on it. The 3d element Cr, Mn, Fe, or Co increases the theoretical strength by up to 10%. Interstitial atoms C, N, and O enhance, but H and B decrease the theoretical strength. This is in agreement with experimental findings that C, O, and N are $\alpha$-phase strengthening elements.
Figures 2 and 3 show that both the bulk modulus and theoretical strength are influenced by the ‘extra’ atoms. As the modulus is reduced by the alloying elements Sc, V, Ni, or Cu, or by the interstitial atoms H or B, the estimated theoretical strength is also decreased. The 3$d$ elements Cr, Mn, Fe, and Co, and the interstitial atoms C, N, and O enhance the bulk modulus, while the theoretical strength is also enhanced by them. To depict the effect, a useful parameter is the relative admissible strain, defined as the ratio of the strength to modulus $\Delta \sigma_{th}/\Delta B$. The admissible strain according to the results of the present calculations is plotted in Fig. 4. From the view point of developing a high strength and lower modulus materials.

4. Conclusions

Based on the calculations of the electronic structure and binding energies of some hypothetical binary α-type titanium alloys and of α-titanium with interstitial atom, the bulk modulus and theoretical strength of considered systems were estimated. The influence of the ‘extra’ (alloying and interstitial) elements on the modulus and theoretical strength was studied under the condition that the ‘extra’ atoms are independent of each other in their contribution to the studied properties. The main conclusions are:

(1) The relative change in theoretical bulk modulus, $\Delta B$, is larger than unity for the alloying elements Cr, Mn, Fe and Co, and the interstitial atoms C, N, and O, but lower for the alloying elements Sc, V, Ni, and Cu, and the interstitial atoms H and B as found in the present study.

(2) The relative change in the strength of titanium with and without the ‘extra’ atom, $\Delta \sigma_{th}$, is larger than unity for the alloying elements Cr, Mn, Fe and Co, and the interstitial atoms C, N, and O, but lower for the alloying elements Sc, V, Ni, and Cu, and the interstitial atoms H and B.

(3) The variation of the admissible strain of α-titanium containing an ‘extra’ atom is that Cr, Mn, Fe, and Co enhance the relative admissible strain, while Sc, V, Ni, and Cu reduce it. All of the interstitial atoms considered here enhance the relative admissible strain to larger than unity.

(4) From the view point of developing a high strength and lower modulus bio-titanium alloy, 3$d$ elements Cr, Mn, Fe, and Co are favorable elements. All of the interstitial atoms considered also have the effect enhancing the relative admissible strain of α-titanium.

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