Investigation of beta Ti-Mo phase stability employing the first principle approach

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Abstract. The improvement for load bearing dental and orthopaedic implants of Titanium (Ti) based alloys have become significant in the medical industry, this is due to the increase of knee and hip replacement amongst younger individuals and the deterioration of body parts by increasing human age. Hence the need for developing low modulus Ti-based alloys with biocompatible properties and low elastic modulus close to that of bone. This study aims to investigate the stability of Ti-based alloys for biomedical applications using the first-principles approach. The stability of β $Ti_{100-x}Mo_x$ (x=0-10) alloys was investigated with respect to their equilibrium lattice parameters, elastic constants and the density of states. The study employed the density functional theory (DFT) within the generalized gradient approximation (GGA). Addition of the alloying element was achieved employing the visual crystal approximation embedded in CASTEP. Interestingly, the Molybdenum (Mo) addition stabilizes the β-phase with an increasing C′ moduli and the density of states suggest that the phase is being stabilized at a higher content of Mo.

1. Introduction

The use of Titanium (Ti) and Ti-based alloys implantable device has become a great part of modern medicine [1]. Compared to other metallic implants (stainless steel and cobalt-chromium) Ti-based alloys stands out with its unique properties which makes it more probable for prosthetic applications [2]. In biomedical applications, Ti and Ti-based alloys are the best choices for replacing or repairing damaged hard tissues such as bone plate, since they have excellent characteristics such as biocompatibility, Osseointegration, high wear, and corrosion resistance, low compatibility issues, and high strength [3]. Ti-alloys also exhibit low modulus of elasticity (100-110 GPa) that is lower compared to other materials but more than that of a bone in the range of (20-40GPa) [4]. Ti-based alloys have become significant in the medical industry due to the increase in knee and hip replacement amongst younger individuals and there has been a dramatic increase of the use of biomedical implants because of the deterioration of body parts by increasing human age. With this rise, the need for the development of Ti-alloys implants that can withstand physiological loads and can serve for a lifetime without failure has become crucial[5].

Most research on titanium alloys for biomedical implantable devices has focused on β-phase Ti- alloys because of the bcc structure. The body centered cubic (bcc) structure can be manipulated to enhance properties such as lower elastic modulus, high wear and corrosion resistance. β-phase Ti alloys containing Mo are the safest alloying metals which has been used for orthopaedic implants applications due to their unique combination of excellent mechanical properties, low elastic modulus, and superior bio-corrosion resistance, low allergenic and non-toxic properties, which give rise to excellent biocompatibility [6-7].

Previous studies have found that elastic modulus can significantly be reduced by adjusting the concentration of β stabilizing element such as Molybdenum [8-9]. Zhao et al [10] investigated β-phase Ti-Mo alloys with changeable Young's modulus for spinal fixation application. In their study it was found that increasing the concentration of Mo the stability of β-phase increases. Further studies done on Ti-Mo binary systems have reported Young's modulus between the ranges of 60-100 GPa which is still not

low enough for biomedical applications [8-10]. There are a few reported studies [8-10] on Ti-Mo for biomedical application, the main objective of this study is to investigate the stability of Ti-Mo alloys with different Mo concentration varying from 0-10% and carry out structural properties such as heats of formation, elastic constants and density of state using first principle approach.

2. Methodology

First principle calculations were performed using Cambridge Serial Total Energy Package (CASTEP) code as implemented in Material Studio [11] based on density functional theory (DFT). The Perdew-Burke-Ernzerhof (PBE) functional of the generalized gradient approximation (GGA) [12] described the electron-exchange and correlation. The CASTEP code performed a variation solution to the Kohn-Sham equations by using a density mixing scheme [13] to minimize the total energy and conjugate gradients to relax the ions under the influence of the Hellmann-Feynman forces. After the convergence test, an energy cut-off of 400 eV and the k-mash of 6x6x6 were chosen since they were sufficient to converge our structures. The Brillouin zone integrations were performed for suitably large sets of *k*-points according to Monkhorst and Pack [14]. The solid solution approach employing visual crystal approximation (VCA) [15] embedded in CASTEP was used to substitute Ti with Mo atoms. It is a much simpler and computationally less expensive approach in which one studies a crystal with the primitive periodicity but composed of fictitious ‘‘virtual’’ atoms that interpolate between the behavior of the atoms in the parent compounds. This technique has seen wide use in band structure calculations [16, 17, 18]

3. Results and Discussions

3.1. Structural and elastic properties of $Ti_{100-x}Mo_x$ *(x: 0, 6, 8, 10)*

3.2. In Fig. 1, the investigated structure is shown which is a β-phase having a space group of Im-3m bcc crystal with two atoms which was generated using tungsten (W) as a prototype. Using VCA the β-phase Ti was doped with Mo as illustrated in fig 1 below. The B2 Ti structure was subjected to full geometry optimization, allowing both the lattice parameters and volume to change. The calculated equilibrium lattice parameters of the structures are shown in Table 1. The β Ti lattice was found to be a=3.165 and in good comparison with the available experimental value of 3.26 [19]. As the Mo content is added on the Ti, the lattice parameter increases as shown in Table 1, which is due to the larger atomic radius of Mo (1.90 Å) than that of Ti (1.76 Å).

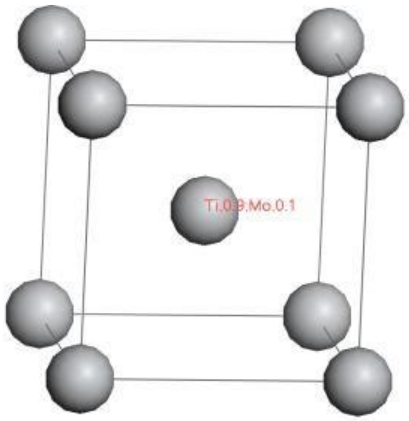

Figure 1: *Structure of β-phase Ti-Mo.*

Table1: The equilibrium lattice parameters and elastic constants for the $Ti_{100-x}Mo_x$ (x: 0, 6, 8, 10)

Structure	Lattice parameter	C_{11}	C_{44}	C_{12}	C′	Y(GPa)
Ti	3.165	96	46	160	-32	
$Ti_{94}Mo_6$	3.233	89	33	112	-11.5	42
$Ti_{92}Mo_8$	3.230	109	35	108	0.5	61
$Ti_{90}Mo_{10}$	3.222	128	36	100	14	75

In addition, the elastic properties of the structures were calculated and are also shown in Table 1. The accurate calculations of elasticity are important for gaining an insight into the mechanical and elastic properties of solids. There are three (C_{11}, C_{12} and C_{44}) independent elastic constants for cubic structure [20]. The mechanical stability criterion given by Born's [20] for a cubic crystal is as follows:

$$C_{11} + 2C_{12} > 0,\ C_{11} > |C_{12}| \text{ and } C_{44} > 0$$

Wherein the C′ is calculated using this equation: $C' = (C_{11}-C_{12})/2$

For a structure to be considered mechanically stable, the stability criterion for the elastic constants should all be satisfied. The pure Ti β is found to be unstable at 0 K with a negative C′ of -32 which is due to the C_{11} being less than C_{12} (i.e. 96 < 160). As the 6 at. % Mo is added, C′ modulus increases but still remains negative. Lower C_{11} reflects weak resistance to shear deformation, which is observed on Table 1 above for Mo concentration less than 6 at. %. The C′ is stabilized at Mo > 8 at % wherein the C_{11} is found to be greater than C_{12}. The calculated Young's modulus exhibits a similar trend to the elastic constants, indicating hardening of C′ which results in high Young's modulus of β-phase with increasing Mo content.

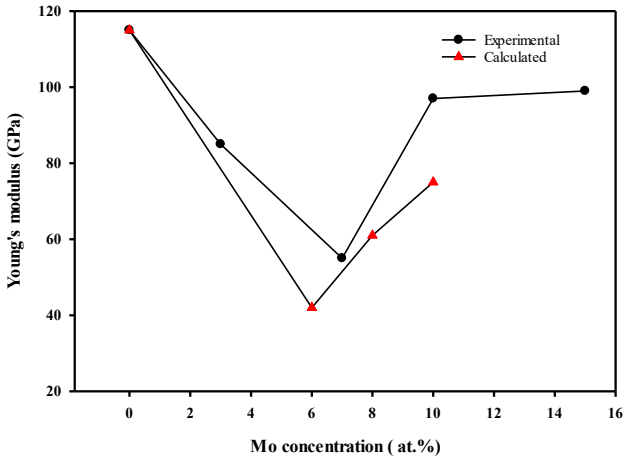

Figure 2: *Experimental [21] and calculated Young's modulus of* $Ti_{100-x}Mo_x$

Figure 2 represent the Young's moduli of the calculated and experimental Ti-Mo with respect to the varying Mo concentration. In fig 2 the experimental Young's modulus decreased with the addition of Mo, although the actual value of the modulus fluctuated with different Mo concentration which was due to the presence of metastable phases α″ and ω in some of the samples during the XRD and TEM investigation [21]. Interestingly the theoretical and experimental Young modulus show a similar trend, they both increase with increasing Mo content showing structural stability. It is also observed that the

Youngs modulus of $Ti_{92}Mo_8$ in the reported study was low (61GPa) which was in good agreement with Sung experimental observations [21]. It is noted that the Young's modulus of the experimental result was larger than that of the theoretical calculations this is because the theoretical calculations were restricted to bulk single crystals, while the real samples are polycrystalline [21-22]. The difference might also be due to the difference in temperature (0K for all calculations and 298K for experimental).

3.3. Density of states

In order to further understand the chemical bonding and β-phase stability, we calculated the DOS of all the $Ti_{100-x}Mo_x$ structures (fig 3). Structural instability is related to the Fermi level (E_f) which is represented by the vertical line in fig 3 below. According to Mahlangu et al [23] structures with the highest and lowest density of states at E_f is considered the least and most stable, respectively. It is very clear from fig 3 that the s and p orbitals peaks are much broader than sharp peaks observed for the d orbital at E_f. We also observe in fig 3b, c and d that d-orbital of Mo has the major contribution to the TDOS near Fermi level.

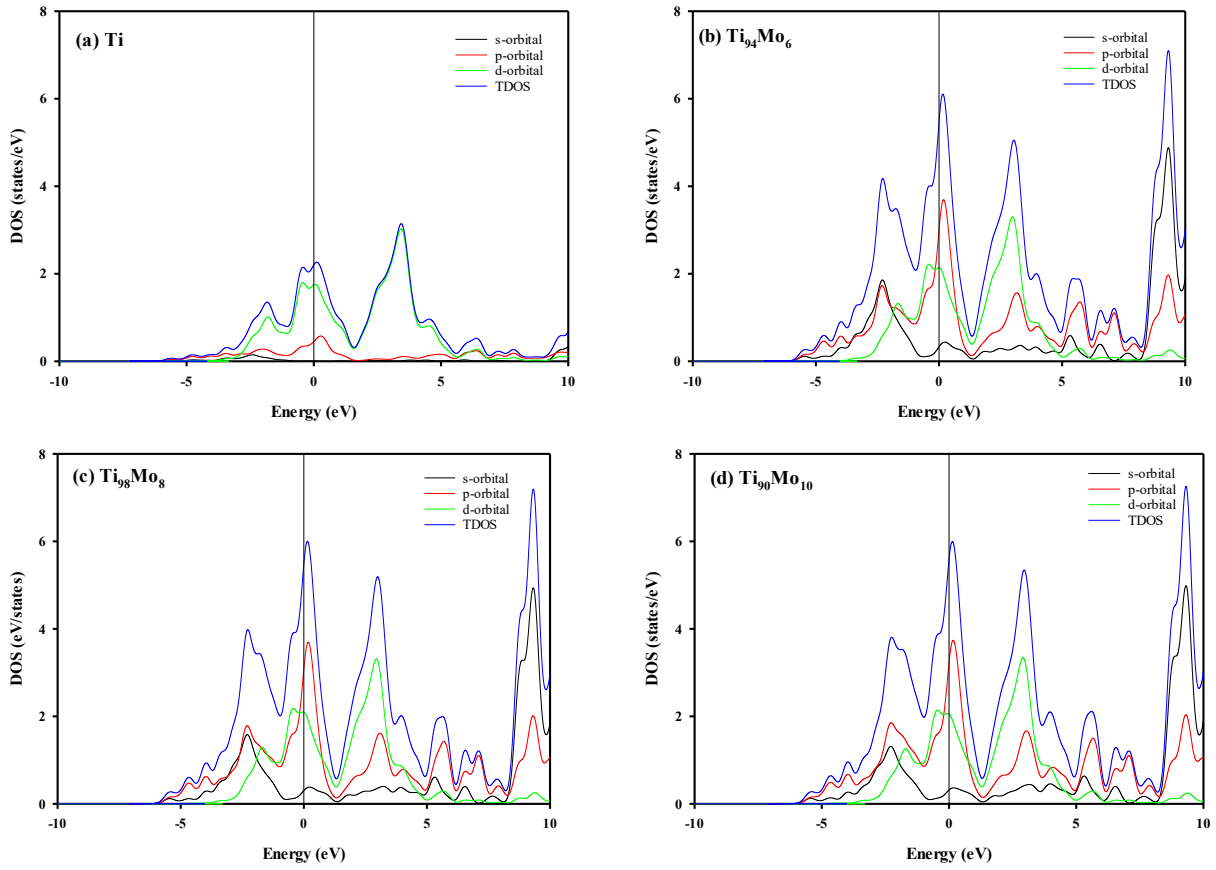

Figure 3: *Density of states curves of β-phase for Ti-Mo alloys with different Mo contents (0-10%).*

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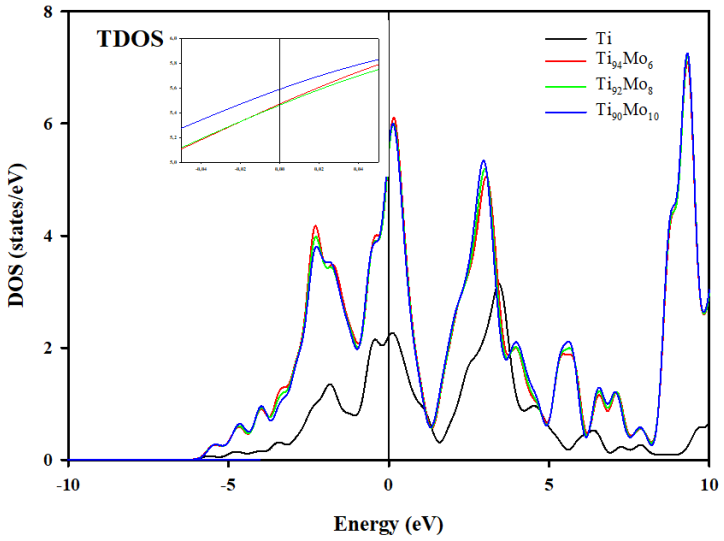

Figure 4: *Total Density of states curves of β-phase for Ti-Mo alloys with different Mo contents (0-10%).*

The embedded total density of states is represented in figure 4. We note that the TDOS peak of pure titanium although with lower density of states near E_f it is much broader than the other peaks and located in the antibonding region. Interestingly at 8 at. % Mo concentration, the dip of the TDOS at E_f was observed to slightly move away from the antibonding region suggesting β-phase stability increased gradually. Lower number of density of states was observed for $Ti_{92}Mo_8$ plot at E_f compared to the other structures confirming it to be the most stable structure. However, it was noted that $Ti_{90}Mo_{10}$ is the least stable structure since it has the highest number of density of states at E_f. Our DOS analysis is in good agreement with some theoretical studies which suggest that the DOS at E_f decreased with increasing Mo content for ordered cells, indicating that the β-phase stability. The opposite is observed for distorted cells where by Li et al observed that higher Mo content produces the most stable structure [24].

4. Conclusions

In this study the stability of Ti-Mo alloys was investigated with respect to their equilibrium lattice parameters, elastic constants and density of states employing DFT embedded in CASTEP code. The lattice parameters were found to be increasing with increase in Mo content. The elastic properties results were found to be in good agreement with the available experimental and theoretical findings. The C′ moduli of β Ti was found to be unstable with a negative value. Interestingly as Mo was added in the system C′ increased resulting in a positive C′ at higher Mo content. It was observed that the elastic constants obeyed the stability criterion since the addition Mo content stabilized the β-phase with an increasing C′ moduli suggesting that the phase is being stabilized at a higher content of Mo. The density of states suggests that the β-phase stabilizes at higher Mo content. As more Mo is added the structure becomes unstable as seen by the highest number of states of the highest content of Mo.

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