Available online at https://doi.org/10.36303/SATNT.2021cosaami.29
Conference of the South African Advanced Materials Initiative

First principles study of phase stability and elastic properties of Ti94Mo6-xZrx (where x: 2 ≤ x ≥ 5) for biomaterials

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Abstract

Elastic modulus is a very important physical aspect for biomaterials which is impartial to various replacements as artificially hip joints, bone plate, and gum implants since it measures the material's resistance to be deformed elastically. This is because "stress shielding effect" will result in the re absorption of natural bone and the implant loosening if a great difference of elastic modulus exists between the biomaterial implant and human bone. In this study first principle calculations have been performed to study the β-phase of Ti-Mo-Zr system to improve its elastic moduli. The phase stability of $Ti_{94}Mo_{6-x}Zr_x$ (where x: 2 - 5) alloys was investigated with respect to their equilibrium lattice parameters, elastic constants and the density of states. The results suggest that the Youngs moduli can be significantly enhanced with the addition of Zirconium (Zr) and decreasing Molybdenum (Mo) concentration while keeping Titanium (Ti) constant, which indicates phase stability. The Youngs modulus of structures $Ti_{94}Mo_{6-x}Zr_x$ was found to be between -2GPa and 24GPa. The electronic density of states curves also showed phase stability for structures $Ti_{94}Mo_4Zr_2$ since it was observed that the Fermi level is located close to the valley of the pseudogap. The results obtained are in agreement with the available experimental data and showed a similar trend. The study has shown that Zr has improved the elastic properties and the phase stability of Titanium alloy.

Keywords: First principle, Titanium alloys, Elastic modulus, Density of states

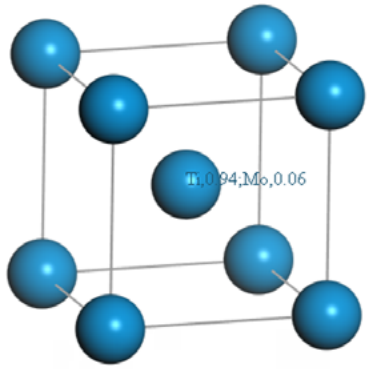
1. Introduction

The development of superior load-bearing biomaterials with good biocompatibility and low elastic modulus is required for an aging population with an active lifestyle. Titanium alloys are excellent biomaterials because of their mechanical characteristics and biocompatibility (Wang 1996). A biomaterial is a material designed to interact with a biological system in order to evaluate, treat, enhance, or replace any human tissue, organ, or function (Geetha et al. 2009). As a result, biomaterials must possess particular characteristics before they may be amended into the human body. Mechanical properties such as stiffness, strength, fracture toughness, wear resistance, fatigue strength, corrosion resistance, and biomedical properties such as toxicity and osseointergration are examples of such characteristics (Wang 1996, Long et al. 1998). Because of the rise in complete knee and hip replacements, there has been a surge of interest in creating better biomaterials for load-bearing implants in recent years. According to (Kurtz et al. 2007), the total number of hip and knee replacements will grow by 174 percent and 673 percent, respectively, from 2005 to 2030, resulting in 572,000 hip and 3.48 million knee surgeries (Kurtz et al. 2007). This rapid growth is the driving factor for the development of improved biomaterial implants.

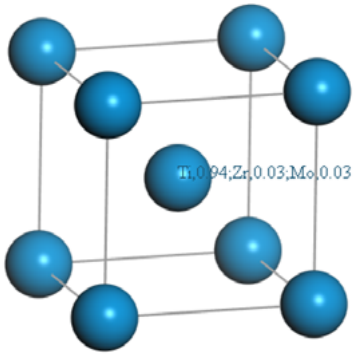
Ti-6Al-4V, stainless steels, commercially pure titanium (CP Ti) and Co-Cr alloys were the most prevalent implants for these purposes in past years due to their excellent mechanical strength and toughness (Hamidi 2017). However, there have been concerns about these materials, such as cytotoxicity in alloys containing aluminum and vanadium (Yu 1993, Okazaki et al. 1996). Another significant hurdle with these common biomaterial implants is stress shielding, which can contribute to implant failure. Stress shielding occurs when there is a mismatch between the elastic modulus of the human bones and implants, in which the metal implant absorbs the bulk of the loads, leaving the more compliant tissue essentially unstressed (Gross and Abel 2001). In this situation, bone will resorb back into the body, a process known as disuse atrophy, which leads to a loss in bone density, and can result in implant loosening and failure (Yu et al. 1993, Okazaki et al 1996, Gross and Abel 2001).

The frequently used biomaterials CP Ti and Ti6Al4V have high elastic moduli of ~100 GPa and ~110-112 GPa, respectively, when compared to human bone (~10-30 GPa) due to the α-phase (Engelbrecht et al. 2013, Ho et al. 2009, Li et al. 2014). The β-phase's elastic modulus is substantially smaller (~60-80 GPa) than the α-phase's (~100-120 GPa) (Engelbrecht et al. 2013, Ho et al. 2009, Li et al. 2014). As a result, the phase plays a significant role in the high elastic modulus of CP Ti and Ti-6Al-4V. Therefore, the phases structure of Ti-based alloys affects their properties, and some phases can be stabilized by adding alloying elements (Ho et al. 2009). The discovery and design of non-toxic metastable β-type Ti alloys with a low young's modulus has received a lot of attention and is our current research focus.

The alloying element of interest for this study is Molybdenum (Mo) and Zirconium (Zr). Mo is a β-phase stabilizing and biocompatible element that has gained a lot of interest and has been added to a lot of β-type Ti-based alloys. Zr, on the other hand, is a material of interest for surgical implants because it has high mechanical strength, biocompatibility, osseointegration, and corrosion



(a)



(b)

Figure 1: Structure of (a) β-phase Ti-Mo and (b) Ti-Mo-Zr

resistance (Li et al 2014). Zr is an excellent choice for alloying since it is a neutral element when dissolved in Ti and can increase alloy strength and elasticity (Zhen and Lian 2006). As a result, based on Density functional theory (DFT) and plane wave pseudo-potentials, we analyze the phase stability of $Ti_{94}Mo_{6-x}Zr_x$ (where x: 2 - 5) alloys with respect to their equilibrium lattice parameters, elastic constants, and density of states.

2. Methodology

First principle calculations were carried out using Cambridge Serial Total Energy Package (CASTEP) code (Segall et al. 2002) as implemented in Material Studio based on density functional theory with the projected augmented wave (Kresse and Joubert 1999). The Perdew–Burke–Ernzerhof (PBE) generalised gradient approximation (GGA) was used to treat the exchange–correlation functional (Perdew and Wang 1992). The cut-off energy 420 eV and an 8x8x8 k-point mesh were used as they were found to be sufficient to converge the structures to a 1meV/atom precision. The Monkhorst–Pack grid was used to integrate the Brillouin zone (Monkhorst and Pack 1976). The energy shift was less than 0.001 eV, hence these values were found to be sufficient for convergence. CASTEP calculations were carried out at 0 K, suggesting that the total energy was equal to the Gibbs free energy for determining phase stability. To substitute Ti atoms with Mo and Zr atoms, the solid solution technique using virtual crystal approximation (VCA) (Ramer and Rappe 2000) embedded in CASTEP was applied.

3. Results and discussions

3.1 Structural and elastic properties of $Ti_{94}Mo_{6-x}Zr_x$

The arbitrary distribution of atoms in a cubic structure model of Ti_{94}-Mo_6 and Ti_{94}-Mo_3-Zr_3 is shown in Figure 1 below. The beta phase structure is a body-centred cubic (BCC) crystal with three atoms and all the lattice parameters are equal i.e., a=b=c. In Table 1, the equilibrium lattice parameters and the elastic constants of $Ti_{94}Mo_{6-x}Zr_x$ are shown. Initially, the binary cubic Ti_{94}-Mo_6 structure was fully optimized with a=3.165 Å. According to table 1 below, the lattice parameter reduces at first and subsequently increases as Zr content increases. In part, this is due to the fact that the atomic radius of Zr (2.04 Å) is larger than both Ti (1.46 Å) and Mo (1.36 Å). The crystal lattice shrinks as a result of introducing Zr to the Ti-Mo system.

In addition, the elastic properties of the structures were calculated and are shown in Table 1. Elastic constants specify a material's elastic properties, which may directly reflect its mechanical properties. For cubic structures, there are three independent elastic constants (C_{11}, C_{12}, and C_{44}). The mechanical stability of a cubic crystal as determined by Born's (1955) criteria is as follows:

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

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

Biomaterials are required to have a high strength and a low elastic modulus. Elastic modulus describes an alloy's capacity to withstand elastic deformation; however, to avoid the stress-shielding effect, the elastic modulus of a biomaterial should be close as possible to that of human bones (~10–30GPa) (Engelbrecht et al. 2013, Ho et al. 2009, Li et al. 2014). In Table 1, the calculated elastic moduli of Ti-Mo-Zr alloys are listed. The elastic modulus of the structure rapidly dropped as the Zr concentration increased, with positive C'. The results revealed that increasing the amount of Zr in the alloy enhanced its elasticity, allowing it to attain a low elastic modulus compatible with human bone. The elastic modulus of the Ti-Mo binary structure was enhanced by adding Zr, which reduced it from 42GPa to as low as -2GPa. In this work, the elastic moduli of Ti-Zr-Mo alloys are lower than those of experimental and existing theoretical alloys used for comparison (Marker 2017, Zhao et al. 2011, Zhao et al. 2011). Zhao et al. (2011). discovered the experimental elastic modulus of $TiMo_{12}Zr_5$ alloy was found to be 64GPa, which is significantly higher than that found in this study with close Zr concentration. This disparity could be explained by the fact that elastic moduli were measured at different temperatures, 0K for the current investigation and 1133K for the experiment. Zhao et al. (2011) also found that the experimental findings show that the Zr and Mo contents have a significant impact on both the microstructures and the elastic properties of the proposed alloys, as seen in this work. The lattice parameters of the Ti-Mo binary structure were 3.233Å and fell to 2.812Å when Zr was added to the system; however, adding more Zr boosted the lattice parameters

Table 1: The calculated equilibrium lattice parameters and elastic constants for the $Ti_{94}Mo_{6-x}Zr_x$ (x: 2-5)

Structure	Lattice parameter (Å)	C_{11}	C_{12}	C_{44}	C'	Elastic modulus (GPa)
$Ti_{94}Mo_6$	3.233	89	112	33	-11.5	42
$Ti_{94}Mo_4Zr_2$	2.812	127	116	32	5.5	24.33
$Ti_{94}Mo_3Zr_3$	2.819	136	121	30	7.5	13.59
$Ti_{94}Mo_2Zr_4$	2.826	144	127	28	8.5	4
$Ti_{94}Mo_1Zr_5$	2.834	158	137	27	10.5	-2

from 2.812Å to 2.834Å, which demonstrated similar trend behavior to other similar theoretical studies (Gong Lai 2011).

Figures 2a and 2b show a comparison between the elastic constants of Ti-Mo-Zr found in this study and those found in previous theoretical studies (Marker 2017). All of the findings were consistent with the dynamic's criterion for crystal structure stability as stated above. As can be seen in Fig. 2a, the elastic constants C_{11} and C_{12} increased as the Zr content increased, while C_{44} decreased. Both figures suggest that phase stability can be achieved with the inclusion of Zr since they have a similar trend, namely that increasing Zr content raises C_{11} and C_{12} while decreasing C_{44}. The estimated C_{11}, C_{12}, and C_{44} for all of the structures, however, were much lower than the experimental and theoretical values (Marker 2017, Zhao 2011, Zhao 2011).

3.2 Density of states

To evaluate the underlying function of how alloying elements impact phase stability, we should examine the total electronic density of state (TDOS) of crystal structures $Ti_{94}Mo_{6-x}Zr_x$ with x= 2, 3, 4 and 5 at.% Zr in Fig 3 below. According to Pettifor et al. (1970), the occupied density of state is linked to the zero-energy Fermi energy level (E_f). The dominance of d-states near E_f has been illustrated below, and this will be utilized to understand the TDOS plot. In a β-phase, E_f should be placed at the valley of the pseudogap, which is between +/- 1meV, for a structure to be regarded stable. However, in this work we found huge peaks in the density of states when the Zr concentration was increase. According to the proposed total density of states curves, the structure for 2 at.% Zr concentration was the most stable of our structures since the valley of the pseudogap is slowly migrating to the energy level, indicating phase stability. As more Zr is added to the system, the pseudogap narrows and the energy increases, weakening the system's covalent bonds and reducing the phase stability.

4. Conclusions

In this study, we investigated the phase stability and elastic properties of $Ti_{94}Mo_{6-x}Zr_x$ (where x: 2-5) alloys using DFT and plane wave pseudo-potentials with respect to their equilibrium lattice parameters, elastic constants, and density of states. The addition of Zr stabilized the β-phase while enhancing the elastic modulus, according to the elastic properties. The elastic modulus was improved from 42GPa to -2GPa, allowing $Ti_{94}Mo_{6-x}Zr_x$ to be used in biomedical applications while avoiding stress shielding effect. Since C_{11} and C_{12} rise with increasing Zr concentration and C_{44} decreases, the resultant elastic constants (C_{11}, C_{12}, and C_{44}) were found to be in good agreement with several theoretical

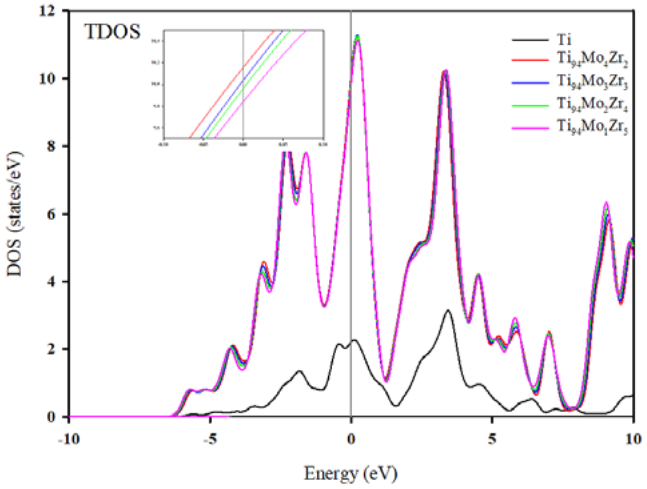


Figure 3: Total Density of states curves of β-phase Ti-Mo-Zr alloys with different Zr contents (2-5 at.%)

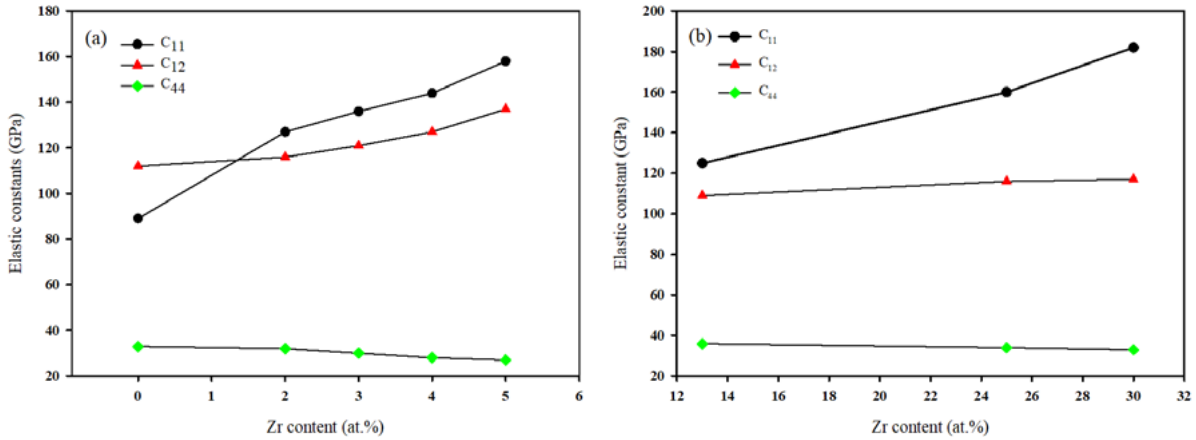


Figure 2: The elastic constants of Ti-Mo-Zr found in this study(a) and those found in previous theoretical studies (b) (Marker 2017)

and experimental data. The density of states plot revealed that the structure for 2 at.% Zr concentration was the most stable of our structures because the valley of the pseudogap was close to the fermi energy level. As a result, since the elastic modulus of $Ti_{94}Mo_4Zr_2$ alloy was discovered to be 24GPa, which is significantly closer to natural bone, this alloy is suitable for biomedical application, reducing bone resorption caused by the stress shielding effect and thus increasing the implants' long-term stability.

Acknowledgements

The authors acknowledge Sefako Makgatho Health Science University and CSIR for their financial support. The support of the CSIR and national research foundation is highly recognised. The calculations were carried out using computer resources at the centre for high-performance computing (CHPC) in Cape Town.

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