Structural, elastic and electronic properties of binary titanium-based shape memory alloys

M E Baloyi[1], R Modiba[2], P E Ngoepe[1] and H R Chauke[1]

[1] Materials Modelling Centre, University of Limpopo, Private Bag X1106, Sovenga, South Africa
[2] Materials Science and Manufacturing, CSIR, PO Box 395, Pretoria, 0001, South   Africa

Email: mphamela.baloyi@ul.ac.za

Abstract. Ab initio density functional theory approach was employed to investigate the structural properties, elastic constant and phonon dispersion of B2 binary TiPt, TiNi and TiCo shape memory alloys. We employed the plane-wave pseudopotential method within generalized gradient approximation parameterized by Perdew, Burke and Enzerhof using VASP code. These alloys have the ability to remember their shapes after deformation, and this is due to their shape memory effect and super elasticity properties. We found that the lattice parameters are in good agreement with the experimental results. Furthermore, the TiPt structure is thermodynamically stable displaying lowest heats of formation. Their calculated elastic constant indicated that TiPt has higher transformation temperature. The Pugh's ratio clearly indicates that all titanium-based binary alloys are ductile (B/G>1.75). Phonon dispersion curves shows that TiCo is vibrational stable and there are acoustic modes observed at the gamma directions while TiPt is not due to the existence of imaginary frequencies observed along M high symmetry direction, in agreement with calculated elastic constants.

1. Introduction

Shape memory alloys (SMAs) have the ability to recover their original shapes after being deformed when heated above certain temperature [1]. They exhibit two interesting properties, shape memory effect and superelasticity. Titanium-based SMAs have attracted significant attention due to its distinctive properties for extensive applications such as actuators and sensors, which are displayed in martensitic transformations [2]. It is well known that most Ti-based alloys have an ordered B2 phase at high temperatures and transform to low temperature martensitic phase (B19/19′) when temperature decreases [3]. TiNi exhibits significant shape memory effect (SME) and Nitinol became the most commonly used SMAs [4]. The development of SMAs which can operate at high temperature is important to improve shape memory properties [5]. An increase of the martensitic transformation of SMAs allows for extending their application range to high temperatures. These alloys possess higher martensitic transformation temperature above 373 K [6]. In addition, elevated temperature SMAs such as Ti(Pt, Pd) are of potential technological interest for elevated temperature SMA applications [5].

Furthermore, B2 TiNi and TiCo have martensitic transformation temperature of 320 K and 40 K, respectively [7, 8, 9]. Platinum have higher temperature of 2041 K which leads to TiPt having the highest martensitic transformation of about 1300 K and exhibit B2 to B19 transformation [10]. In this paper, we

investigate the phase stability of TiPt, TiNi and TiCo alloys at 50:50 equiatomic composition using the heats of formation, elastic properties, electronic properties (density of states) and phonon dispersion curves of B2 structures. We found that B2 TiPt is unstable at low temperature, in agreement with experimental findings. Our results also show that B2 TiCo is stable with no soft modes observed. However, TiCo has shown potential for alloy development, being elastically and vibrationally stable.

The structures of TiPt is shown in figure 1 below. It is a cubic B2 structure also known as a high temperature beta phase with the space group of Pm-3m. Its experimental equilibrium lattice parameter is 3.192 Å [11]. The lattice parameter of the cubic B2 TiNi and TiCo are reported to be 3.015 Å [12] and 2.988 Å [9], respectively. All the structures have a B2 CsCl prototype structure.
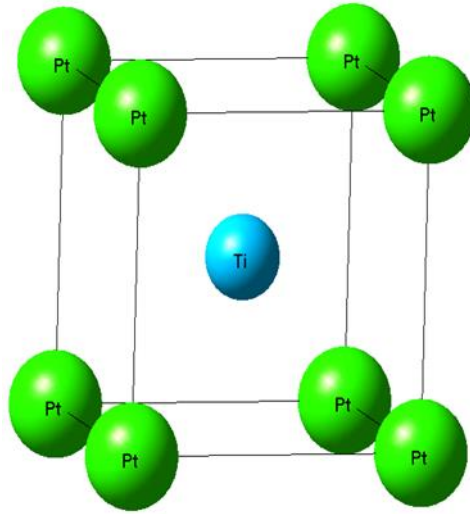

Figure 1. The cubic phase TiPt binary alloys at 50:50 equiatomic composition.

2. Methodology

The calculations were carried out using ab initio density functional theory (DFT) [13] formalism with the projector augmented wave (PAW) [24], as implemented in VASP code [14]. An energy cutoff of 500 eV was used, to achieve a good convergence of the parameters. For exchange-correlation functional, the generalized gradient approximation of Perdew, Burke and Enzerhof (GGA-PBE) [15] was chosen. Interactions in the Brillouin zone were performed with special k-spacing of 0.2 with accordance to Monkhorst and Parck scheme [16]. The phonon dispersion spectra were evaluated using PHONON code [17] as implemented in Materials Design within MedeA software of VASP code [14].

3. Results and discussion

3.1. Equilibrium lattice parameter

In Table 1; calculated equilibrium lattice parameters and heats of formation for the B2 Ti-based binary alloys are shown. The equilibrium lattice parameter results are in good agreement with the experimental findings. Heats of formation is used to predict the stability of alloys and in constructing their phase diagrams [18]. The equation for determining heats of formation (ΔH_f) is given by [23]:

$$\Delta H_f^{Ti-M} = \frac{1}{n} E^{Ti-M} - [(1-x)E^{Ti} + xE^M] \tag{1}$$

where E^{Ti-M} is the total energy of alloy, E^{Ti} is the total energy of Ti, E^M is the total energy of element M=Pt, Co, Ni, n is the total number of atoms and x is the fractional concentration of the constituent element. The lowest and highest heats of formation show the most and least stable material, respectively.

TiPt is found to be more stable with the lowest heats of formation of -0.821 eV/atom while that of TiNi was found to be the least stable with the highest value of -0.403 eV/atom.

Table 1. Equilibrium lattice parameters (Å) and heats of formation ΔH_f (eV/atom) of B2 TiPt, TiNi and TiCo.

Structures	a	ΔH_f
TiPt	3.180 (3.192) [a]	-0.821
TiCo	2.994 (2.988) [b]	-0.527
TiNi	3.011 (3.015) [c]	-0.403

[a] reference [11]
[b] reference [9]
[c] reference [12]

3.2.   Elastic constants

We have also calculated the elastic constants C_{ij}, Anisotropy (A) and Pugh's ratio (B/G) for cubic phases as shown in Table 2. For us to understand the martensitic transformation of these alloys, we investigate their elastic properties [7]. The stability criterion for the cubic system to be mechanically stable are as follows [19];

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

The elastic moduli are then calculated based on the three independent elastic constants in equation (2) above:

$$C' = \frac{C_{11} - C_{12}}{2} \text{ and } A = \frac{C_{44}}{C'}, \tag{3}$$

where C′ is shear modulus and *A* is the anisotropy factor [20]. TiPt fails to satisfy the criterion shown in equation (2), $C_{11} < C_{12}$ leading to a negative C′ of -32 GPa. Hence, B2 TiPt is mechanically unstable at 0 K. B2 TiCo and TiNi satisfy all the cubic stability criterion and these alloys are considered to be mechanically stable. Lower C_{44} value of 44.07 GPa of TiCo signals that the C_{44} shear resistance becomes comparable to the C′ shear resistance, resulting in low anisotropy value of 1.72 which give rise to monoclinic B19′ martensite [7]. Therefore, TiCo undergoes the B2 to B19′ martensitic transformation due to its lower *A*. These results are consistent with the experimental findings [3]. Higher *A* indicates the higher transformation temperature, B2 to B19 transformation. Calculated *A* of TiNi with a value of 2.52 agrees with the experimental value of 2.4 [12]. In addition, *A* of TiCo agrees to within 3% the experimental with value 1.72 (1.84) [21]. The bulk (B) and shear (G) moduli are calculated to investigate ductility of these alloys. The investigated binary alloys are found to be ductile since B/G>1.75 [22].

Table 2. Lattice parameters (Å), elastic constants (GPa) and heats of formation (eV/atom) of TiPt, TiNi and TiCo binary alloys.

Structures	C_{11}	C_{12}	C_{44}	C′	*A*	B/G
TiPt [d]	145	210	45	-32		2.20
TiCo	266.89	215.73	44.07	25.58	1.72 (1.84) [e]	3.35
TiNi	190.32	143.97	58.36	23.18	2.52 (2.40) [f]	5.57

[d] reference [19]
[e] reference [21]
[f] reference [12]

3.3. Phonon dispersions

We have performed the phonon dispersions calculations on structures and the plots are shown in figure 2. Soft modes are observed at the M and R high symmetry direction indicating the instability of TiPt. Phonon density of states (PDOS) suggest that the soft modes observed are due to high vibration of Pt atom. In addition, our phonon dispersion calculations show TiNi to be unstable since there are soft modes observed in the phonon curves. These soft modes are observed along M directions and this could be attributed to high vibration of Ni atoms as shown on the phonon DOS. TiCo is found to be vibrationally stable with no soft modes observed, in agreement with predicted elastic constants where we observed a lower A as compared to the other structures.
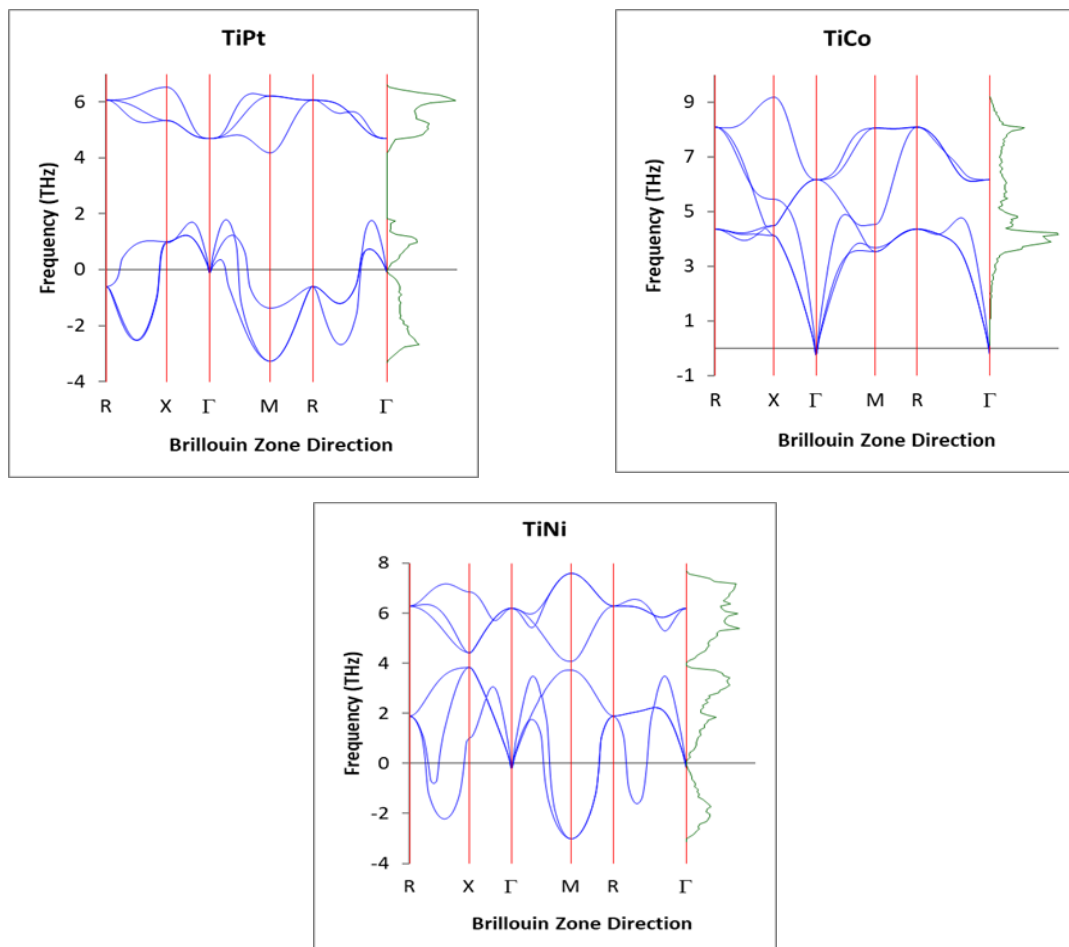

Figure 2. Phonon dispersion curves and Phonon density of states of TiPt, TiNi and TiCo binary alloys.

3.4. Electronic density of states

In figure 3, the total (tDOS) and partial density of states (PDOS) of TiPt, TiNi and TiCo binary alloys are shown. DOS of the alloys indicates the stability with respect to their behavior at the Fermi level E_f. The structure with highest and lowest DOS at the E_f is considered least and most stable, respectively. Shapes of all tDOS curves are similar comprising of two set of peaks separated by a pseudo-gap. The lower tDOS peaks are occupied by Pt for TiPt, Co for TiCo and Ni for TiNi, and the higher tDOS peaks are mainly due to the d state of Ti atoms. TiCo has the lowest Ti d DOS value of 1 states per eV at the E_f, indicating the stability of these alloys. In addition, TiPt is the least stable alloy due to its higher Ti d

DOS value of 1.6 eV at the E_f. Our DOS results agree with our calculated elastic constant, showing that TiCo is the most stable structure.
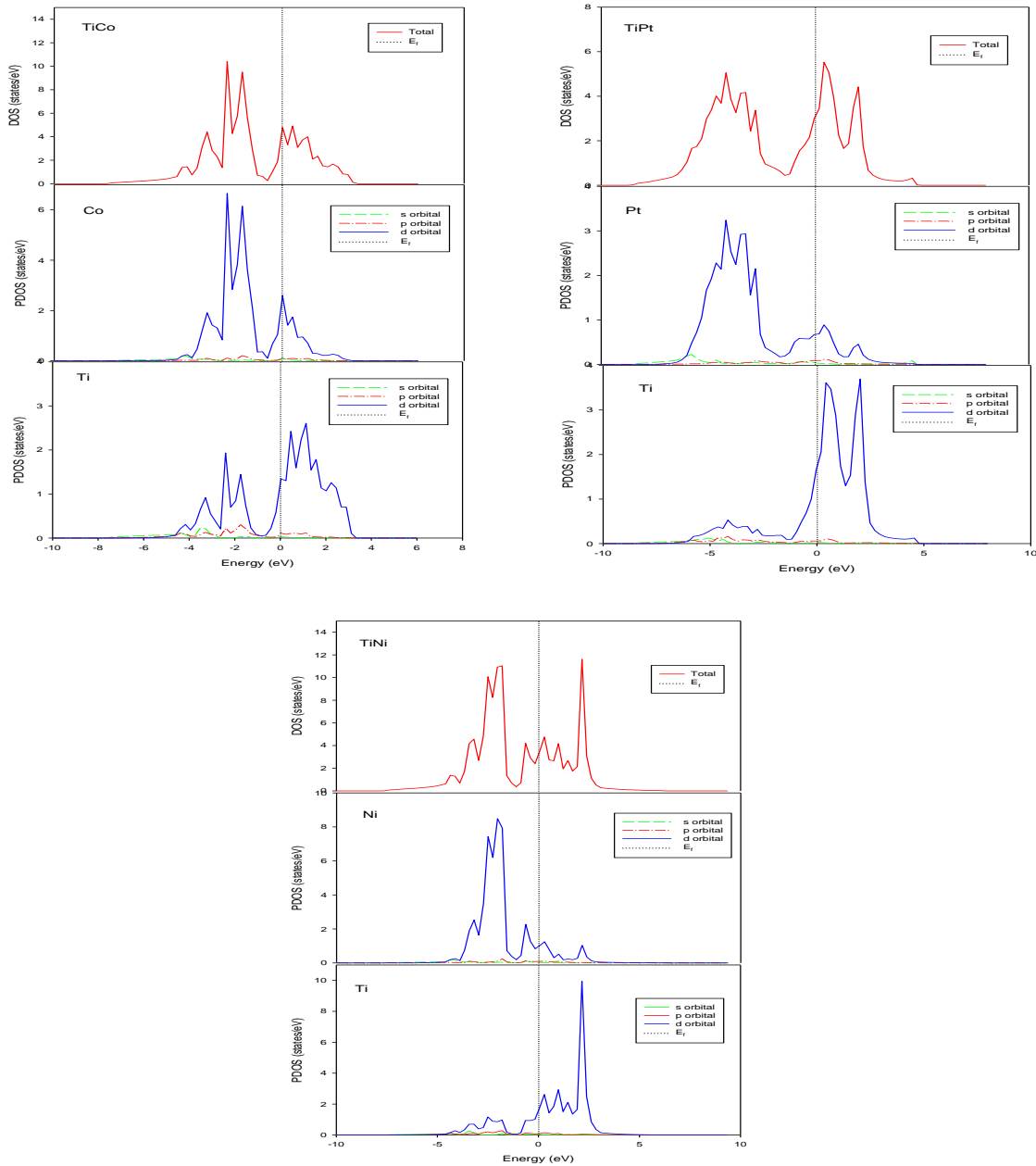

Figure 3. Total and partial density of states of TiCo, TiPt and TiNi binary alloys. The Fermi level is at the value of 0 eV.

4. Summary and conclusion

The equilibrium lattice parameters, heats of formation, elastic properties and electronic properties of equiatomic B2 TiCo, TiNi and TiPt were determined using the first principle calculations. Our results are in agreement with the experimental findings within 3 %. We note that the predicted heats of formation confirm the stability of binary alloys investigated. Calculated elastic constants show that TiPt

is mechanically unstable at low temperature whereas TiCo and TiNi are mechanically stable. It is interesting to note that TiCo is vibrationally stable with no soft modes observed, in agreement with the predicted heats of formation and elastic constants. Only TiCo is energetically, mechanically and dynamically stable according to the calculations, performed at zero temperature and pressure.

Acknowledgements

References

[1] Mahlangu R, Chauke H R and Ngoepe P E 2014 *Advanced Material Science* **1019** 385-390
[2] Lagoudas D C and Hartl D J 2007 *J. Aerospace Engineering* **221** 535-549
[3] Chang-Long T, Wei C and Jing-Chuan Z 2006 *Chin. Phys. Lett.* **23** 2863-2866
[4] Strittmatter J and Gumpel P 2009 *Australian J. Mech. Eng.* **7** 99-109
[5] Yamabe-Mitarai Y and Wadood A 2014 *Mater. Sci. Eng. A* **601** 106-110
[6] Yamabe-Mitarai Y, Arockiakumar R, Wadood A, Suresh K S, Kitashima T, Hara T, Shimojo M, Tasaki W, Takalashi M, Takalashi S and Hosoda H 2015 *Materials Today* **2S** 517-522
[7] Biggs T, Cornish L A, Witcomb M J and Cortie M B 2004 *J. of Alloys and Compounds* **375** 120-127
[8] Xu K, Huang X M, Lu J, Lui H S, Cai G and Jin Z P 2018 *Calphad* **60** 191-199
[9] Wadood A, Takalashi M, Takalashi S, Hosoda H and Yamabe-Mitarai 2013
[10] Miyazaki S and Ishida A 1999 *Mater. Sci. Eng. A* **273-275** 106-133
[11] Kresse G and Hafner J 1994 *Phys. Rev. B* **49** 251-269
[12] Nishida M, Matsuda M, Yasumoto Y, Yano S, Yamabe-Mitarai Y and Hara T 2013 *Mater. Sci. Tech.* **24** 884-889
[13] Tan C L, Tian X H, Ji G J, Gui T L and Cai W 2008 *Solid State Communications* **147** 8-10
[14] Kresse G and Hafner J 1993 *Phys. Rev. B* **47** 558561
[15] Perdew J P, Burke K and Enzerhof M 1996 *Phys. Rev. Lett.* **77** 88-92
[16] Monkhorst H J and Pack J D 1976 *Phys. Rev. B* **13** 88-92
[17] Parlinski K, Li Z Q and Kawazoe Y 1997 *Phys. Rev. Lett.* **78** 4063-4066
[18] Hennig R G, Carlsson A E, Kelton K F and Henley C L 2005 *Phys. Rev. B* **71** 100-103
[19] Mahlangu R, Phasha M J, Chauke H R and Ngoepe P E 2013 *Intermetallics* **33** 27-32
[20] Phasha M J, Ngoepe P E, Chauke H R, Pettifor D G and Nguyen-Mann D 2010 *Intermetallics* **18** 2083-2089
[21] Lin Y S, Cak M, Paidar V and Vitek V 2012 *Acta Mater.* **60** 881-888
[22] Pugh S F 1954 *J. Sci.* **45** 823-843
[23] Fernando G W, Watson R E and Weinert M 1992 *Phys. Rev. B* **45** 15 8233
[24] Blöchl P E 1992 *Phys. Rev. B* **50** 17953-17979