

***Ab Initio* Study of $\text{Ti}_{50}\text{Pt}_{50-x}\text{Hf}_x$ ($x = 6.25, 18.75, 25$) Potential Shape Memory Alloys**

M E Baloyi¹, R Modiba², P E Ngoepe¹ and H R Chauke¹

¹Materials Modelling Centre, University of Limpopo, Private Bag X1106, Sovenga, South Africa

²Future Production: 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 study the effect of Hf addition to the TiPt binary shape memory alloys (SMAs). SMAs have the ability to retain their original shapes after deformation when heated above a certain temperature. They have been widely used in the fields of engineering and medicine due to their shape memory effect (SME) and super-plasticity which are displayed in martensitic transformations. In this work, a supercell approach method in VASP was used to substitute Pt with 6.25, 18.75 and 25 at.% Hf in the TiPt. The calculated heats of formation predicted that 6.25 at.% Hf to be the most stable structure and the elastic properties showed that $\text{Ti}_{50}\text{Pt}_{50-x}\text{Hf}_x$ is mechanically stable for all the concentrations. It is seen that hafnium addition stabilizes the B2 TiPt with all the C_{ij} 's being positive. Moreover, phonon dispersion curves indicate that increasing the Hf content in the system stabilizes the structure.

1. Introduction

Shape memory alloys (SMAs) have the ability to recover their original shape after being deformed when heated above a certain temperature. They exhibit two interesting properties, shape memory effect (SME) and superelasticity [1]. Titanium-based SMAs have attracted significant attention due to its distinctive properties for extensive applications such as actuators and sensors [2]. TiNi has been extensively studied for various applications because it exhibits significant shape memory effect (SME) and excellent superelasticity [3]. However, some NiTi applications are greatly limited by its low martensitic transformation temperatures, T_m , lower than 373 K [4]. The development of SMAs which can operate at high temperature has been studied to improve SME properties and application areas [5].

High-temperature shape memory alloys (HTSMAs) with T_m greater than 373 K have numerous potential applications. TiPt and TiPd alloys are potential alloys to be used at high temperature due to their high T_m [6]. Moreover, TiPt has a higher T_m of about 1300 K rendering it suitable for HTSMAs development [7]. Previously, density functional theory (DFT) results on TiPt showed B2 phase to be unstable at 0 K due to negative C' shear modulus [8, 9]. In order to enhance the shape memory properties and stability of TiPt, ternary alloys are being considered. In the previous work, Zr, Ru, and Co were reported to enhance the shape recovery ratio [10]. However, martensitic transformation temperature of TiPt decreased with the addition of the Zr, Ru, Co and V [11, 12, 13].

In this work, the density functional theory (DFT) technique was used to demonstrate the effect of alloying elements (Hf) on the stability in $\text{Ti}_{50}\text{Pt}_{50-x}\text{M}_x$ shape memory alloys. Stabilities of B2 $\text{Ti}_{50}\text{Pt}_{50-x}\text{Hf}_x$ ($x = 6.25, 18.75, 25$) were investigated with respect to their equilibrium lattice parameters, heats of

formation, elastic and vibrational properties of the structures. 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 equilibrium lattice parameter is 3.192 Å. The supercell with 16 atoms was built using substitutional search embedded in MedeA and Pt atoms substituted with 6.25, 18.75, and 25 at.% Hf.

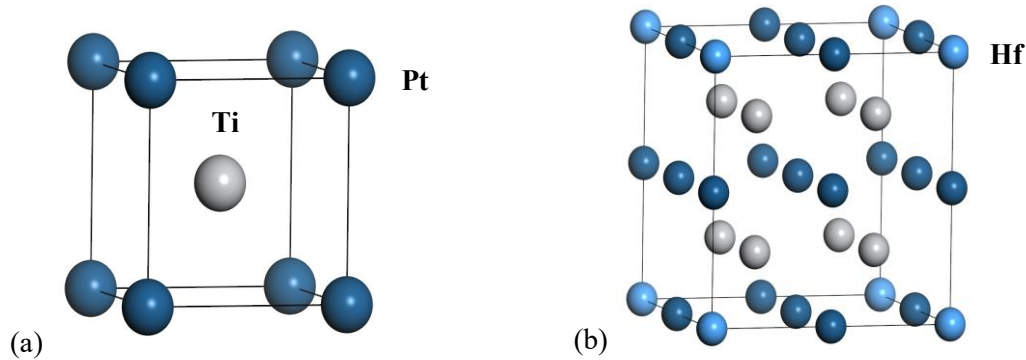


Figure 1. The atomic arrangement unit cell of (a) B2 TiPt system with a space group Pm-3m. Supercell of 2X2X2 for (b) B2 TiPt-Hf structures with 16 atoms.

2. Methodology

The calculations were carried out using *ab initio* density functional theory (DFT) [14, 15] formalism as implemented in the Vienna *ab initio* simulation package VASP [16] with the projector augmented wave (PAW) [17]. An energy cut-off of 500 eV was used, as it was sufficient to converge the total energy of the cubic B2 TiPt alloys. For the exchange-correlation functional, the generalized gradient approximation of Perdew, Burke, and Enzerhof (GGA-PBE) [18] was chosen. The Brillouin zone integrations were performed for suitably large sets of k -points according to Monkhorst and Pack [19]. A 2X2X2 supercell of cubic B2 TiPt with 16 atoms was used. The substitutional search tool embedded in VASP was used to substitute Pt with Ta. The phonon dispersion spectra were evaluated using PHONON code [20] as implemented in MedeA software.

3. Results and discussion

3.1. Structural and thermodynamic properties

The calculated DFT results on equilibrium lattice parameters and heats of formation of the $\text{Ti}_{50}\text{Pt}_{50-x}\text{Hf}_x$ ($x = 6.25, 18.75, 25$) are shown in Table 1. The calculated results show that the partial substitution of Pt with Hf increases the lattice parameters of the $\text{Ti}_{50}\text{Pt}_{50-x}\text{Hf}_x$. This implies that the structure becomes larger in volume. The volume of the structures increases since the atomic radius of Hf is larger than that of Ti and Pt atoms. The lattice parameters obtained for the ternary alloys are comparable to lattice parameter obtained by Bozollo *et al* [21] at 5 at.% Hf ($a=3.17$ Å).

Heats of formation were calculated to determine the stability of the structure. The equation for determining heats of formation (ΔH_f) is discussed by Baloyi *et al* [22]. The lowest and highest heats of formation show the most and least stable material, respectively. $\text{Ti}_{50}\text{Pt}_{43.75}\text{Hf}_{6.25}$ is found to be the most stable with the lowest predicted ΔH_f of -0.82 eV/atom. The systems become less favourable as the Hf content increases to 18.75 and 25 at.%, which indicates that the phase stabilities of the structures become worse (unstable).

Table 1. Lattice parameters (a) and heats of formation (ΔH_f) of the $\text{Ti}_{50}\text{Pt}_{50-x}\text{Hf}_x$ ternary alloys.

Structures	Lattice parameter (Å)	ΔH_f (eV/atoms)
$\text{Ti}_{50}\text{Pt}_{50}$ [8]	$a = 3.18$	-0.796
$\text{Ti}_{50}\text{Pt}_{43.75}\text{Hf}_{6.25}$	$a = 3.19$	-0.82
$\text{Ti}_{50}\text{Pt}_{31.25}\text{Hf}_{18.75}$	$a = 3.22$	-0.54
$\text{Ti}_{50}\text{Pt}_{25}\text{Hf}_{25}$	$a = 3.25$	-0.50

3.2. Elastic constants

The elastic constants (C_{ij}), anisotropy (A) and Pugh's ratio (B/G) of $\text{Ti}_{50}\text{Pt}_{50-x}\text{Hf}_x$ alloys were calculated as shown in Table 2. The elastic properties investigation is considered in this study to understand the martensitic transformation behaviour of these alloys [11]. The mechanical stability criterion of a cubic crystal is given as [8, 23]:

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

The positive C' designates the mechanical stability of the crystal, otherwise unstable. Elastic constants of the B2 structures are positive, thus satisfying mechanical stability criteria set for cubic crystals. Therefore, B2 structures are mechanically stable. $\text{Ti}_{50}\text{Pt}_{25}\text{Hf}_{25}$ are considered to be anisotropic since A is approximately 1 ($A \approx 1$, a less micro crack in the material). To investigate the ductility of these alloys, bulk (B) and shear (G) moduli are considered. All ternary alloys in this study are ductile due to Pugh's ratio greater than the critical value ($B/G > 1.75$) [24].

Table 2. Elastic properties of $\text{Ti}_{50}\text{Pt}_{50-x}\text{Hf}_x$ ($x = 6.25, 18.75, 25$) ternary alloys and their anisotropy A .

Elasticity (GPa)	$\text{Ti}_{50}\text{Pt}_{50}$ [8]	$\text{Ti}_{50}\text{Pt}_{43.75}\text{Hf}_{6.25}$	$\text{Ti}_{50}\text{Pt}_{31.25}\text{Hf}_{18.75}$	$\text{Ti}_{50}\text{Pt}_{25}\text{Hf}_{25}$
C_{11}	145	189	197	196
C_{12}	210	175	151	124
C_{44}	45	53	53	67
C'	-32	7	23	36
$A = 2C_{44}/(C_{11}-C_{12})$		7.48	2.26	1.87
B/G		7.34	4.44	2.82

3.3. Phonon dispersions

Phonon dispersion calculations were performed to investigate the vibrational properties of $\text{Ti}_{50}\text{Pt}_{50-x}\text{Hf}_x$ ternary alloys at different concentration and are shown in Figure 2. In this section, we deduce the influence of Hf on the presence of soft modes in the negative frequency of TiPt binaries by the way of phonon dispersion and phonon DOS. These curves display interesting behaviour as we increase Hf concentration in the system. $\text{Ti}_{50}\text{Pt}_{43.75}\text{Hf}_{6.25}$ is unstable due to observed vibrations in the negative frequency along with the high symmetry directions, displayed by phonon dispersion curves. The observed soft modes are due to the high vibration of Pt atoms in the system. The vibrations are observed at a frequency of approximately -2 THz. The soft modes observed are along R, M, X and Γ directions on the phonon spectra. It is interesting to note that at higher content of Hf ($x = 18.75$ and 25), the material becomes vibrationally stable with no soft modes observed on the phonon dispersion

curves in the negative frequency. $\text{Ti}_{50}\text{Pt}_{31.25}\text{Hf}_{18.75}$ and $\text{Ti}_{50}\text{Pt}_{25}\text{Hf}_{25}$ are vibrational stable due to the absence of soft modes in the negative frequency of phonon dispersion curves. These results show that as Hf content increases in the system, the material becomes stable which is in good agreement with the predicted elastic constants.

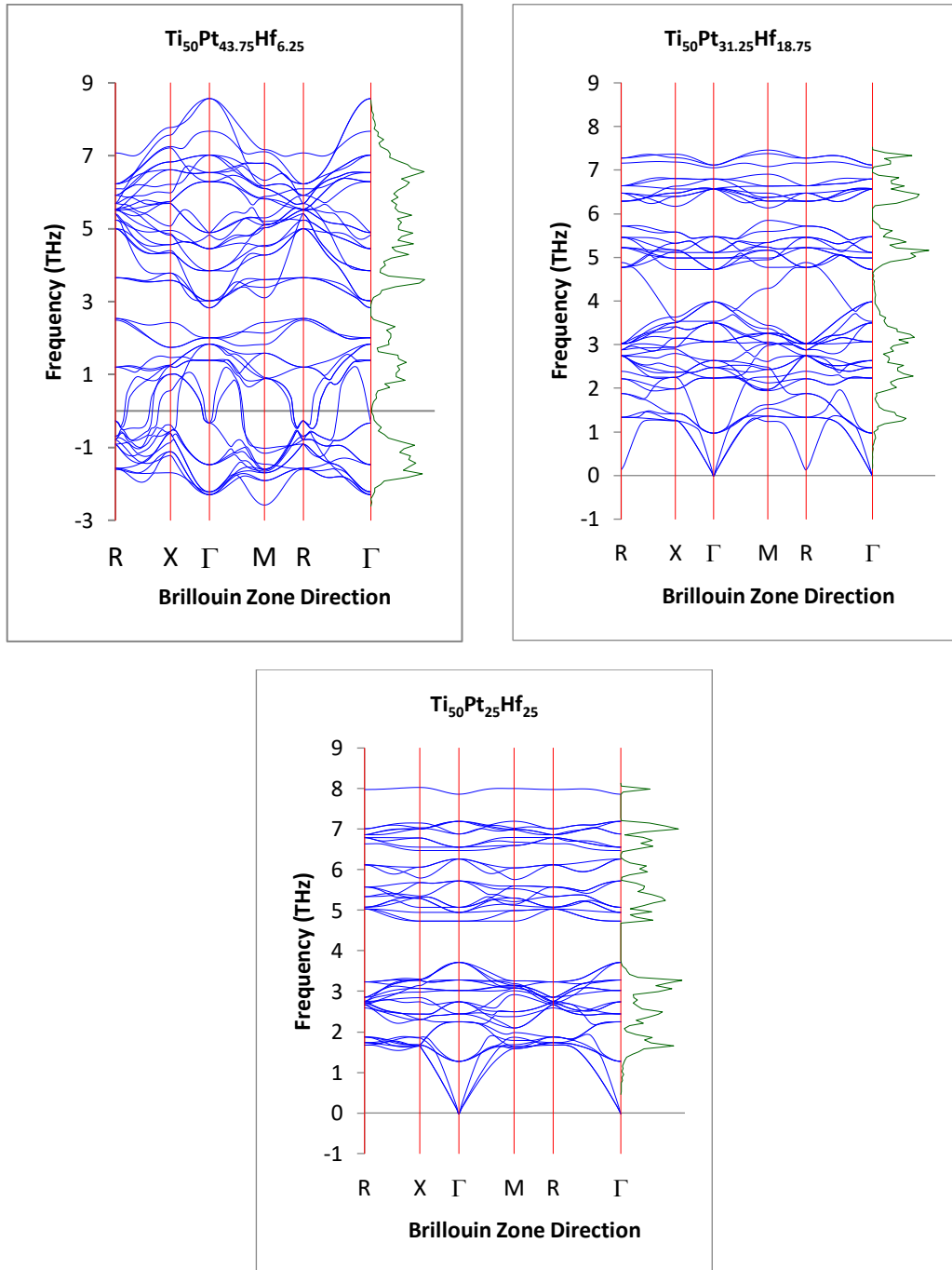


Figure 2. Phonon dispersions of $\text{Ti}_{50}\text{Pt}_{50-x}\text{Hf}_x$ ($x= 6.25, 18.75, 25$) ternary alloys.

4. Summary and conclusion

A first principle approach was used to study the stability of the $\text{Ti}_{50}\text{Pt}_{50-x}\text{Hf}_x$ atomic composition using the supercell approach. The ternary structures were found to be thermodynamically stable with $\text{Ti}_{50}\text{Pt}_{43.75}\text{Hf}_{6.25}$ being the most stable (lowest heats of formation). Elastic constants showed the stability of $\text{Ti}_{50}\text{Pt}_{50-x}\text{Hf}_x$ since all the C_{ij} 's were found to be positive and obey the elastic stability criterion of the cubic lattice. Interestingly, all the ternary alloys under study are ductile. $\text{Ti}_{50}\text{Pt}_{43.75}\text{Hf}_{6.25}$ was found to be vibrationally unstable due to observed soft modes at the negative frequency, whereas at 18.75 and 25 at.% Hf the system becomes more stable. Phonon dispersion curves predicted the stability of ternaries as Hf content increases. TiPtHf has shown potential for high temperature shape memory alloy (HTSMA) development since the alloy displayed elastic and vibrational stability properties.

Acknowledgements

I would like to thank NRF and CSIR for financial support. The work was carried at the Materials Modelling Centre, University of Limpopo and the Centre for High performance computing (CHPC) in South Africa. The support of the South African Research Chair Initiative of the Department of Science and Technology, DST is highly recognized.

References

- [1] Mashamaite M P, Chauke H R and Ngoepe P E 2018 *Material Sci. and Eng.* **430** 012022
- [2] Kubo H, Hamabe A and Shimizu K 1975 *Scr. Metall.* **9** 1083-1087
- [3] Chang-Long T, Wei C and Jing-Chuan Z 2006 *Chinese Phys. Lett.* **23** 2863-2866
- [4] Otsuka K and Kakeshita T 2002 *MRS Bull.* **27** 91-100
- [5] Van Humbeeck J 1999 *Mater. Sci. Eng. A* **273–275** 134-148
- [6] Otsuka and X. Ren 2005 *Prog. Mater. Sci.* **50** 511-678
- [7] Yamabe-Mitarai Y et al. 2015 *Materials Today: Proceedings* **2S** S517-S522
- [8] Mahlangu R, Phasha M J, Chauke H R, Ngoepe P E 2013 *Intermetallics* **33** 27-32
- [9] Baloyi M E, Modiba R, Chauke H R and Ngoepe P E 2018 *Material Sci. and Eng.* **430** 012020
- [10] Takahashi Y, Inamura T, Sakurai J, Hosoda H, Wakashima K and Miyazaki S 2004, *Trans. MRS-J.* **29** 3005–3008
- [11] Chauke H R, Mashamaite M, Modiba R and Ngoepe P E 2017 *Key Eng. Materials* **770** 230-238
- [12] Chikosha S, Mahlatji M L, Modiba R and Chikwanda H K 2018 *Material Sci. and Eng.* **430** 012020
- [13] Modiba R, Baloyi E, Chikosha S, Chauke H R and Ngoepe P E 2018 *Material Sci. and Eng.* **430** 012021
- [14] Hohenberg P and Kohn W 1964 *Phys. Rev. B* **136** 864-871
- [15] Kohn W and Sham L J 1965 *Phys. Rev. A* **140** 1133-1138
- [16] Kresse G and Hafner J 1993 *Phys. Rev. B* **47** 558-561
- [17] Blöchl P E 1994 *Phys. Rev. B* **50** 17953-17979
- [18] Perdew J P, Burke K and Enzerhof M 1996 *Phys. Rev. Lett.* **77** 88-92
- [19] Monkhorst H J and Pack J D 1976 *Phys. Rev. B* **13** 5188-5192
- [20] Parlinski K, Li Z Q and Kawazoe Y 1997 *Phys. Rev. Lett.* **78** 4063-4066
- [21] Bozollo G, Mosca H O and Noebe R D 2007 *Intermetallics* **15** 901-911
- [22] Zhou X W and Zimmerman J A 2008 *Phys. Rev. Lett.* **23** 704-718
- [23] Zhang J M and Guo G Y 1997 *Phys. Rev. Lett.* **78** 4789-4792
- [24] Pugh S F 1954 *J. of Physics*, **45** 823-843