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Computational modelling of $Ti_{50}Pt_{50-X}V_x$ potential shape memory alloys

R Modiba[1,2,*], E Baloyi[2], S Chikosha[1], H R Chauke[2] and P E Ngoepe[2]

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

*Rmahlangu1@csir.co.za

Abstract. The demand for shape memory alloys for high temperatures have increased in recent years and TiPt alloys are promising candidates. The martensitic transformation temperature of TiPt is higher with the value of approximately 1300 K as compared to the commercialised TiNi which transforms at 300 K. Titanium-based SMAs 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. Some of the applications include actuators and medical stents. Previous studies showed that the alloy is mechanically unstable with the negative C′ modulus at 0 K. In this work, supercell approach is used to substitute Pt with vanadium on the B2 TiPt structure and evaluate the mechanical stability of the structures. The equilibrium lattice parameters, elastic properties and the phonon dispersions were calculated to investigate the stability of the $Ti_{50}Pt_{50-X}V_X$. Interestingly the vanadium addition was found to be stabilising the TiPt with all the C_{ij}′s being positive.

1. Introduction

Shape memory alloys (SMAs) are alloys that are capable of shape recovery when exposed to a certain critical temperature after deformation [1] . This is due to a reversible thermoelastic martensitic transformation [2] , which leads to the properties of shape memory effect (SME) and superelasticity (SE). These properties make SMAs useful in applications such as sensors, actuators, microcontrollers, and as biomedical devices [1] [3] [4] [5] [6]. $Ti_{50}Ni_{50}$ is the most commercially successful SMA with a B2-B19' martensitic transformation. The alloys' transformation temperature (TT) can be varied between 100-500 K through careful selection of alloying element(s), often this is also accompanied by changes in crystal structure of the martensite phase [7]. It has long been established experimentally [8] and later theoretically [9] that this composition dependence of TT and martensite crystalline structure can be directly attributed to elastic properties, i.e. the softening and coupling of C' and C_{44} shear modes in the B2 cubic phase during cooling towards TT. First-principles approach, based on elastic constants and electronic structure, has been successfully used to explain the experimentally observed relationships between TT, martensite phase stability, and chemical composition for a number of $TiNi_{50-x}$-M_x alloys (M = Cu, Fe, Pt, Pd; $0 \leq x \leq 25$ at.%) [10] [11].

There has been growing interest to develop solid state actuators for applications in aeronautic and aerospace propulsion technologies with transformation temperatures in the range of 500-1300 K [12], this is beyond the capability TiNi-based alloys. Several binaries such as TiPt, TiIr, TaRu and NbRu

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[12] [13] [14] are good candidates. In the current work, TiPt binary, with a B2-B19 martensitic TT of 1273 K [12] has been considered. However, the alloy exhibits poor shape recovery due to low strength of the B2 austenite phase as well as the absence of two-stage yield behaviour in stress-strain tests conducted below martensite finish temperature (M_f) [15]. There is a need to improve TiPt mechanical properties while maintaining high TT. Solid solution strengthening has been considered as one possible strengthening mechanism, previous work has shown that partial substitution of Pt with Ru and Co, and to a lesser extent Ir, in equiatomic TiPt improves strain recovery while maintaining high TT (M_s > 1000 K) [16].

Previous study on binary TiPt employing density functional theory (DFT) showed B2 phase to be unstable at 0 K with a negative C' modulus [17]. In a process analogous to the one followed for TiNi-based alloys, the current work uses first-principles to investigate the elastic constants and electronic structure of B2 phase in relation to martensitic TT and phase stability in TiPt-based alloys. We present results on the effect of partial substitution of Pt with V on the equiatomic cubic TiPt system using the supercell approach. Stability of the structures of B2 $Ti_{50}Pt_{50-x}V_x$ (x=6.25, 18.75 and 25 at.%) is determined with respect to their equilibrium lattice parameters, elastic constants and phonon dispersions using the DFT approach.

2. Methodology

The calculations were carried out using *ab initio* density functional theory (DFT) [18] [19] formalism as implemented in the Vienna *ab initio* simulation package VASP [20] with the projector augmented wave (PAW) [21]. 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 and Wang (GGA-PBE) [22] was chosen. The Brillouin zone integrations were performed for suitably large sets of *k*-points according to Monkhorst and Pack [23]. 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 V. The phonon dispersion spectra were evaluated using PHONON code [24] as implemented by Materials Design within their MedeA software. All the calculations were done at 0 K.

3. Results and discussion

3.1 Elastic properties

In Table 1 we show the calculated lattice parameters and elastic constants of the $Ti_{50}Pt_{50-x}V_x$ (x = 6.25, 18.75, 25). The calculated results show that as we increase the V concentration in the system the lattice parameter decreases. This is understood since the atomic radius of V (1.71 Å) is less than that of Pt (1.77 Å).

Table 1. Lattice parameters (a) Å, elastic properties C_{ij} (GPa) and anisotropy A of the $Ti_{50}Pt_{50-x}V_x$ ternaries.

Structures	**a**	C_{11}	C_{12}	C_{44}	C'	A
TiPt [17]	3.19	145	210	45	-32	
$Ti_{50}Pt_{43.75}V_{6.25}$	3.156	231	166	49	32	1.52
$Ti_{50}Pt_{31.25}V_{18.75}$	3.123	304	120	48	92	0.52
$Ti_{50}Pt_{25}V_{25}$	3.121	255	131	78	62	1.26

The accurate calculation of elasticity is important in determining the mechanical stability and elastic properties of any system. There are three (C_{11}, C_{12}, C_{44}) independent elastic constants for cubic structures. The mechanical stability criteria of cubic system as outlined elsewhere [17] [25] is given as follows:

$$C_{44} > 0,\ C_{11} > |C_{12}| \quad \text{and} \quad C_{11} + 2C_{12} > 0 \tag{1}$$

Wherein the anisotropy is given by

$$A = \frac{C_{44}}{C'} \tag{2}$$

In order for the structure to be considered stable, the stability criterion for the elastic constants should be satisfied. In principle, positive C' indicates a mechanically stable crystal, otherwise it is unstable. It is interesting to note that all the independent elastic constants C_{11}, C_{12} and C_{44} are positive in the entire range of V compositions. Previous work on pure structures of TiPt at 0 K showed that the B2 structure was unstable with C' shear modulus of -32 GPa, while the C_{44} non-basal shear modulus is positive [17]. This implies that the C' modulus went through zero, transitioning from positive to negative at the transformation temperature, whereas the C_{44} remained positive throughout the phase transition. It follows from the above that the anisotropy ratio (A) must have increased towards a very large number at the transformation temperature, an indication of uncoupling between the C' and C_{44} shear. Upon addition of 6.25 at.% of V, the C_{11} becomes greater than C_{12}, resulting in a positive C'. This suggests mechanical stability of the B2 $Ti_{50}Pt_{43.75}V_{6.25}$ phase in accordance with the stability criterion of the elastic constants [17]. Similar trend is observed for 18.75 and 25 at.% V additions on the TiPt with all the C_{ij}'s being positive.

The anisotropy (A) of β-type martensitic alloys is typically in the range of 3 or greater [26]. Such alloys tend to form martensite characterised by basal plane stacking order structure as is the case with B19 martensite. The anisotropy calculated in the current work for 6.25, 18.75 and 25 at.% V alloys is considerably smaller, suggesting strong coupling between C' and C_{44} shear moduli, and thus a tendency of the B2 phase to transform into B19′ martensite as proposed by Ren and Otsuka [8]. It has been established that the C_{44} modulus controls B19′ TT in compositions with low-value anisotropy. From table 1, it can be observed that there is an overall hardening of C_{44} modulus with increasing V content. This indicates reduction in transformation temperature with V addition.

3.2 Phonon dispersions

Phonon dispersion curves and phonon density of states (DOS) for the $Ti_{50}Pt_{50-x}V_x$ (x = 6.25, 18.75 and 25) were calculated and are shown in Figure 1. The dispersion relations exhibit two types of phonons namely the optical and acoustic modes corresponding to the upper and lower sets of curves in the diagram, respectively. Upon analysis of the phonon dispersion spectra, the structure is considered stable if all the phonon frequencies are positive. However, if some of the phonon frequencies are imaginary, the system is considered unstable [17]. The most negative mode is called the soft mode. Previously, the phonon dispersion curves of the binary B2 phase were reported where the phonon spectra were mostly characterized by the soft modes attributed to the negative value of shear modulus C′ [17]. The phonon dispersion curves of the $Ti_{50}Pt_{43.75}V_{6.25}$ are unstable, displaying soft modes along the high symmetry directions. These soft modes have the lowest frequency at approximately -2.5 THz mainly due to Pt contributions. Interestingly, at higher content of vanadium the structures becomes vibrationally stable with no soft modes observed on the phonon curves below the negative frequency. This findings suggest that V content greater than 18.75 vibrationally stabilises the B2 TiPt phase in agreement with the elastic constants wherein the values of A for 18.75 and 25 at.% are slightly smaller compared to the $Ti_{50}Pt_{43.75}V_{6.25}$ structure. Stabilization of the B2 phase is associated with reduction in martensitic transformation temperature as previously indicated by analysis of elastic constants.

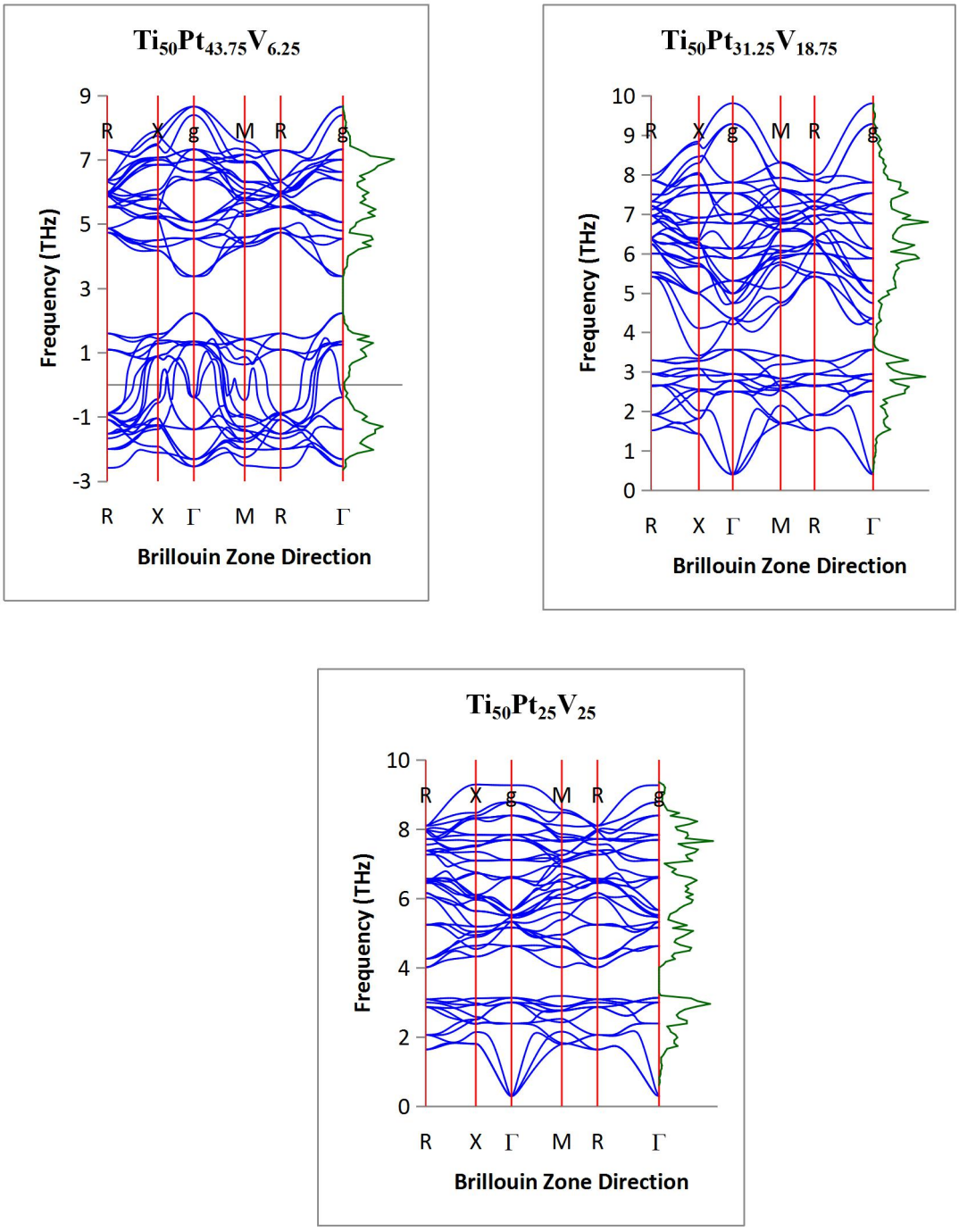


Figure 1: *Phonon dispersion curves for the $Ti_{50}Pt_{43.75}V_{6.25}$, $Ti_{50}Pt_{31.25}V_{18.75}$ and $Ti_{50}Pt_{25}V_{25}$.*

4. Conclusions

Computational modelling study on the elastic properties and phonon dispersion curves of the $Ti_{50}Pt_{50-x}V_x$ (6.25, 18.75, 25) were performed. The addition of V content in TiPt cubic phase was found to be increasing the C' moduli of the TiPt phase leading to all the C_{ij}'s being positive. The elastic constants were found to be stable with all the moduli obeying the elastic stability criterion. Interestingly the calculated anisotropy A of the structures is found to be less than 2 suggesting a B2 to B19´

transformation. The phonon dispersion of the 18.75 and 25 at.% of V were found to be vibrationally stable with no soft modes observed below the negative frequency. The investigations suggest a B2 to B19′ transformation with the TiPt martensitic transformation temperature being lowered.

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