Computational modelling of $Ti_{50}Pt_{50-x}M_x$ shape memory alloys (M: Ni, Ir or Pd and x = 6.25-43.75 at.%)

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

[1] Materials Science and Manufacturing, CSIR, PO Box 395, Pretoria, 0001
[2] Materials Modelling Centre, University of Limpopo, Sovenga, 0727

The *ab initio* density functional theory approach was employed to study the effect of Ni, Ir or Pd addition to the TiPt shape memory alloy. The supercell approach in VASP was used to substitute Pt with 6.25, 18.75, 25.00, 31.25 and 43.75 at.% Ni, Ir or Pd in the B2 TiPt structure. The mechanical stability from elastic properties and phonon dispersion calculations of these alloys were then evaluated. Results suggest that Ni addition reduced the transformation temperatures of the TiPt alloy as indicated by an increase in shear modulus C′. Ir addition increased the martensitic transformation temperature of TiPt, since it gave the lowest shear modulus values at both 18.75 and 25 at.% Ir. However, a high addition of Pd ($x \geq 25$) decreased the transformation temperature of the B2 to B19 TiPt.

INTRODUCTION

Although they have been around for over half a century, new applications continue to be developed for shape memory alloy (SMAs) (Duerig *et al.*, 1990). Titanium-based SMAs have been widely used in the fields of engineering and medicine due to their shape memory effect (SME) and superplasticity which are displayed in martensitic transformations (Wu and Schetky, 2000). Some of the applications include actuators and medical stents (Wu and Schetky, 2000; Otsuka and Kakeshita, 2002; Van Humbeeck, 1999; Duerig, Pelton, and Stockel, 1999). A wide range of alloys are known to exhibit the shape memory effect, which occurs when a material returns to, or 'remembers', its original shape after being heated and deformed. However, the only SMAs of commercial importance are those that can recover substantial amounts of strain, or generate significant force upon changing shape (Duerig *et al.*, 1990). Well-known SMAs include nickel titanium (NiTi), nickel titanium copper (NiTiCu), copper aluminium nickel (CuAlNi), but many other metallic alloy systems also contain SMAs (Otsuka and Wayman, 1998). Many aspects of the transformation are still not well understood (Otsuka and Ren, 2005; Cai *et al.*, 1999*)* even though many theoretical and experimental studies have been devoted to these extraordinary phenomena.

Recently, studies have shown that there is a growing need for SMAs that can be used at higher temperatures (Firstov, van Humbeeck, and Koval, 2004; Kim *et al.*, 2011), but only a few SMAs have the potential to be high-temperature shape memory alloys (HTSMAs). However, as the martensitic transformation temperature T_m of TiPt, at approximately 1273 K (Donkersloot and van Vucht, 1970), is much higher than most other SMAs, TiPt is of potential technological interest for elevated temperature SMA applications. TiPt also undergoes a B2 (β-TiPt) to B19 (α-TiPt) martensitic phase transformation on cooling, at approximately 1323 K (Donkersloot and van Vucht, 1970; Yamabe-Mitarai *et al.*, 2006, 2010), as shown on the Ti-Pt phase diagram in Figure 1 (Biggs *et al.*, 2004). However, experimental work on equiatomic Ti-Pt based alloys (Yamabe-Mitarai *et al.*, 2006, 2010) suggests that there is a very minor shape memory effect due to low critical stress for slip deformation compared to the stress required for martensitic transformation.

Therefore, there is a need to improve the stability and shape memory properties of the TiPt alloys for use at higher temperatures. In this work, the effect of substituting Pt with 6.25 to 43.75 at.% Ni, Ir or Pd on the cubic B2 TiPt using density functional theory (DFT) (Hohenberg and Kohn, 1964)is investigated.
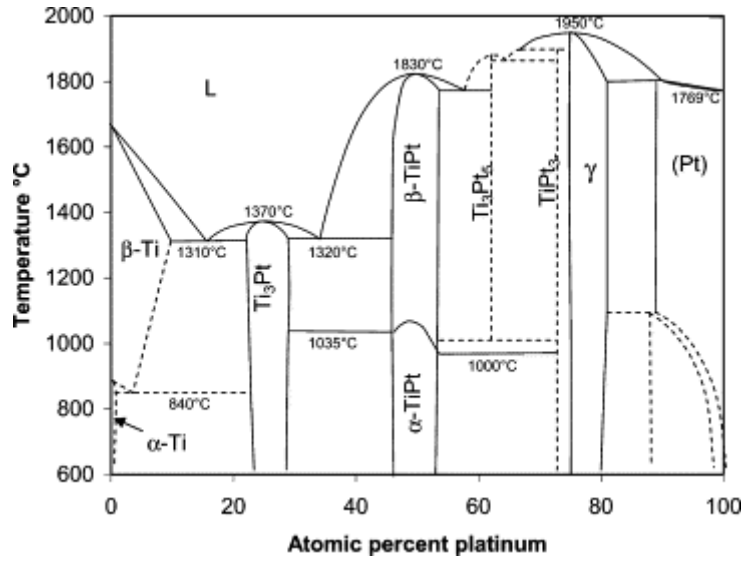
Figure 1. Binary Ti-Pt phase diagram. The area of interest is around 50 at.% Pt where the low-temperature α-TiPt (B19) phase and the high-temperature β-TiPt (B2) phase exist (Biggs et al., 2004).

METHODOLOGY

The calculations were carried out using *ab initio* density functional theory (DFT) formalism as implemented in the VASP total energy package (Kresse and Hafner, 1993, 1994; Kresse and Furthmüller, 1996a, 1996b) with the projector augmented wave (Blöchl, 1994). An energy cutoff of 500 eV was used, as it was sufficient to converge the total energy of the PtTi systems. For the exchange-correlation functional, the generalised gradient approximation of Perdew and Wang (GGA-PBE) (Perdew, Burke and Ernzerhof, 1996) was chosen. The Brillouin zone integrations were performed for suitably large sets of *k* points according to Monkhorst and Pack (1976). For the elastic constants, a *k*-spacing of 0.2 was used for the structures. The calculations were performed at 0 K.

RESULTS AND DISCUSSION

The calculated equilibrium lattice parameters and elastic properties of $Ti_{50}Pt_{50-x}M_x$ are listed in Table I. For B2 TiPt, the previously calculated lattice parameter of 3.19 Å (Mahlangu *et al.*, 2013) agreed with the experimental results. The size of the cubic B2 $Ti_{50}Pt_{50}$ phase decreased as the amount of added Ni or Ir increased. This can be understood since the atoms of Ni and Ir are smaller than those of Pt. However, addition of Pd had a very small effect on the lattice parameter, as its atomic radius is closer to that of Pt.

The heats of formation (H_f) for the structures were also calculated and are shown in Figure 2a-c. Heats of formation of compounds and associated entropies provide the basis for understanding and constructing phase diagrams wherein the lowest value suggest the stability of the phase and the highest value is associated with the instability (Semalty, 2006; Ng and Sun, 2005; Hennig *et al.*, 2005; Mahlangu, 2009). The heats of formation can be estimated by:

$$H_f = E_c - \sum_i x_i E_i \qquad\qquad [1]$$

where E_c is the calculated total energy of the compound and E_i is the calculated total energy of element i in the compound.

B2 TiPt was the most stable phase with the lowest H_f of -0.80 eV. When Ni was added to the TiPt system, the heats of formation increased linearly, reaching -0.38 eV for an alloy with 43.75 at.% Ni. The value of H_f at this concentration was similar to the experimental result of -0.35 eV for NiTi (Moser *et al.*, 2006; Guo and Kleppa, 2001), which is understandable since there was more Ni in the system than Pt. The same trend was observed for both Ir and Pd addition where the heats of formation increased with increasing alloying addition. Interestingly, the heats of formation for the $Ti_{50}Pt_{50-x}Ir_x$ fluctuated with an increase in the Ir content. The results suggest that as the third element (Ni and Pd) is added in the TiPt system, the structures become unstable with their H_f increasing, whereas an Ir addition does not have a linear effect. The H_f for the 6.25 and 18.75 at.% Ir increases and remains constant at 25 at.%Ni. At 31.25 at.% there is an increase observed, and a decrease at 43.75 at.%, as shown in Figure 2b.

The calculated elastic constants of the structures are also listed in Table I. The accurate calculation of elasticity is important for determining the mechanical stability and elastic properties of any system. There are three (C_{11}, C_{12}, C_{44}) independent elastic constants for cubic. The mechanical stability criteria of the cubic system (Mayer *et al.*, 2003)are given as follows:

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

where the shear modulus C' and anisotropy A can be calculated using the following relationships:

$$C' = \frac{1}{2}(C_{11} - C_{12}) \tag{3}$$

$$A = \frac{C_{44}}{C'} \tag{4}$$

The independent elastic constants C_{11}, C_{12} and C_{44} were positive for all the compositions. However the C' of $Ti_{50}Pt_{50-x}M_x$ increased with an increase in Ni content and became stable with $C_{11} > C_{12}$ for both 31.25 at.% Ni and 43.75 at.% Ni alloys. The C' shear modulus of $Ti_{50}Pt_{43.75}Ni_{6.25}$ was -19.5 GPa and increased as the Ni content was increased in the TiPt system. The shear modulus C' of $Ti_{50}Pt_{25}Ni_{25}$ was -2 GPa, which is greater than the -18.5GPa of 18.75 at.% Ni, and it is more stable than 6.25 and 18.75 at.% Ni. Since the C' of the 25 at.% Ni alloy is smaller but negative, this suggests that B2 has transformed to B19 (Ren *et al.*, 1999). According to the literature the origin of the B19′ phase is a result of the coupling between C_{44} and C' as proposed by Ren *et al.* (1999). The C_{44} can be understood to be related to resistance to {001}[100] shear for cubic crystals which is just the non-basal monoclinic shear required by B19′ martensite. Therefore, C_{44} is crucial for the formation of B19′ martensite and controls the transformation temperature of B2 to B19′ (Ren *et al.* (2001). The softening of the {001}[100] basal plane shear modulus C' (Zener, 1947)is able to reasonably explain the parent, cubic B2, to orthorhombic B19 martensitic transformation in several alloys, such as NiAl and CuZn. As C' controls the transformation temperature of B2 to B19, a lower C' shear modulus suggests a higher transformation temperature. The C' moduli of $Ti_{50}Pt_{18.75}Ni_{31.25}$ and $Ti_{50}Pt_{6.25}Ni_{43.75}$ were positive, with anisotropy A values of 7.5 and 2.6 respectively. It is argued that a higher A would be sufficient for the B2 to B19 martensitic transformation, whereas a lower A suggest a B2 to B19′ transformation. An alloy containing 31.25 at.% Ni, would have a B2 to B19 transformation with a larger anisotropy $A=7$, and an alloy with 43.75 at.% Ni ($A=2$) would show a B2 to B19′ transformation.

The calculated results of the elastic constants for the $Ti_{50}Pt_{50-x}Ir_x$ alloys are also shown in Table I. It is observed that the shear modulus C_{44} increases with an increase in Ir concentration. C_{11} is less than C_{12} for all the concentrations, which suggests mechanical instability of the phases. The C' increased to -3 GPa with 6.25 at. % Ir addition and then decreased to values below that of TiPt with further increase in Ir content. This means that the C' of $Ti_{50}Pt_{50-x}I_x$ at concentrations of at.% Ir $\geq$ 18.75 was more unstable than that of TiPt (-32). Ir at these concentrations may increase the transformation temperature of $Ti_{50}Pt_{50-x}Ir_x$, which is understandable since the melting temperature of Ir is high (2719 K). Smaller additions of Ir ($x<18.75$) would reduce the transformation temperature of the alloy, whereas higher contents ($x>18.75$) would increase it.

In the $Ti_{50}Pt_{50-x}Pd_x$ alloys, C' increased with an increase in the Pd concentration similar to the behaviour observed for the $Ti_{50}Pt_{50-x}Ni_x$ alloys. However, the C' value of $Ti_{50}Pt_{43.75}Pd_{6.25}$ is lower than that of TiPt,

which suggests that the transformation temperature would be higher than for TiPt. The transformation temperatures decreased with Pd additions greater than 25 at.%.

Table I. Lattice parameter, a (Å) and elastic constants (GPa) of the $Ti_{50}Pt_{50-x}M_x$ (M: Co, Ni, Ir, Pd) ternaries and their anisotropy A.

| Alloy (at.%)	Lattice parameter	Elastic constants			Shear modulus	Anisotropy
	a	C_{11}	C_{12}	C_{44}	C'	A
TiPt [22]	3.1800 (3.1920) [11]	145	210	45	-32	
$Ti_{50}Pt_{43.75}Ni_{6.25}$	3.1528	162	201	54	-19	
$Ti_{50}Pt_{31.25}Ni_{18.75}$	3.1169	155	192	44	-18	
$Ti_{50}Pt_{25}Ni_{25}$	3.0924	173	177	49	-2	
$Ti_{50}Pt_{18.75}Ni_{31.25}$	3.0907	187	174	53	7	7.5
$Ti_{50}Pt_{6.25}Ni_{43.75}$	3.0625	195	159	47	18	2.6
$Ti_{50}Pt_{43.75}Ir_{6.25}$	3.1698	189	194	31	-3	
$Ti_{50}Pt_{31.25}Ir_{18.75}$	3.1586	129	235	44	-53	
$Ti_{50}Pt_{25}Ir_{25}$	3.1534	104	253	66	-75	
$Ti_{50}Pt_{18.75}Ir_{31.25}$	3.1361	107	265	69	-79	
$Ti_{50}Pt_{6.25}Ir_{43.75}$	3.1318	54	290	79	-118	
$Ti_{50}Pt_{43.75}Pd_{6.25}$	3.1718	116	222	1	-53	
$Ti_{50}Pt_{31.25}Pd_{18.75}$	3.1697	129	202	23	-37	
$Ti_{50}Pt_{25}Pd_{25}$	3.1699	142	192	35	-25	
$Ti_{50}Pt_{18.75}Pd_{31.25}$	3.1695	144	183	43	-20	
$Ti_{50}Pt_{6.25}Pd_{43.75}$	3.1615	147	175	48	-14	
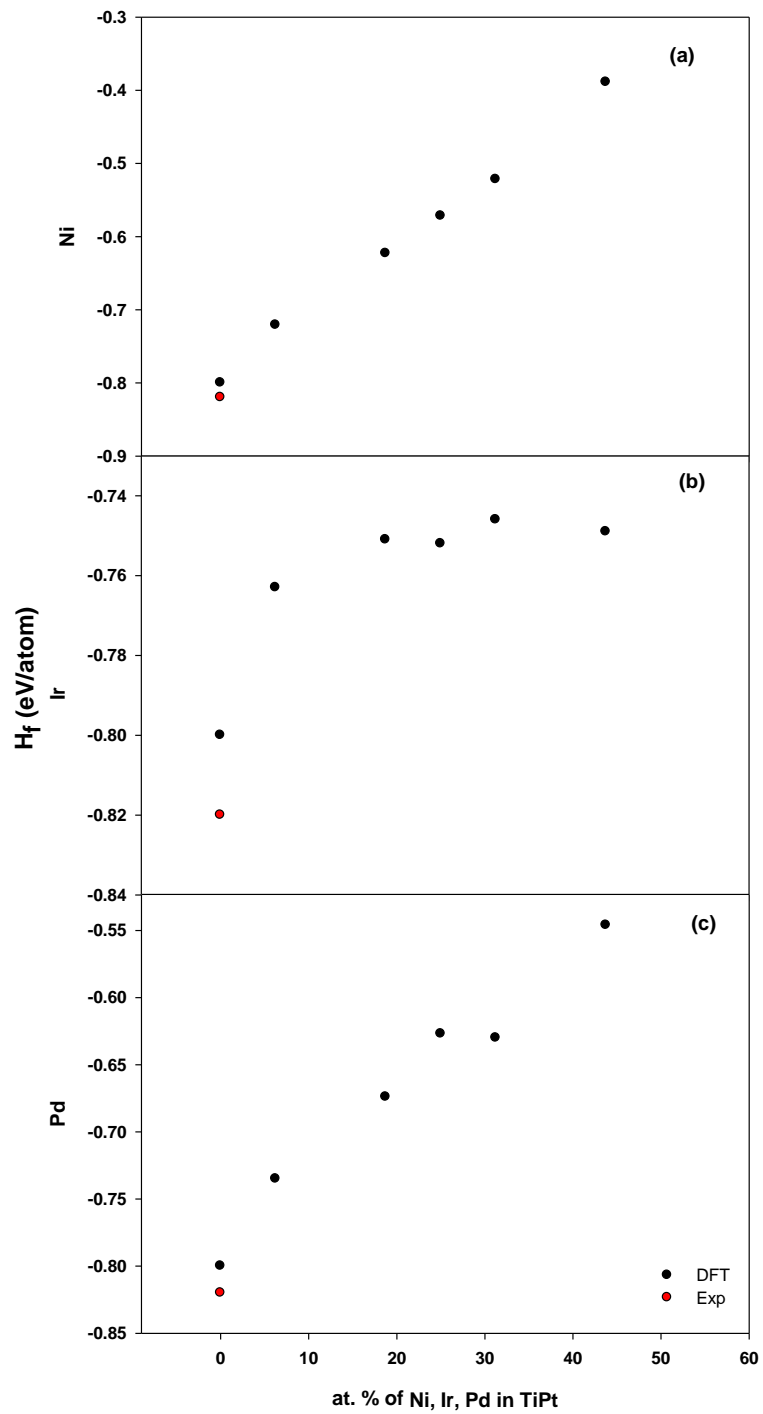
Figure 2. The effect on heats of formation with the substitution of Ni, Ir and Pd on the Ti$_{50}$Pt$_{50-x}$M$_x$ (M: Ni, Ir, Pd, x = 6.25- 43.75).

CONCLUSIONS

A DFT study of the effect of substituting Pt with Ni, Ir and Pd on the cubic B2 TiPt phase was conducted. The results suggest that TiPt becomes unstable with the addition of Ni, Ir and Pd as suggested by the heats of formation wherein the H_f values increased with an increase in the Ni, Ir and Pd concentrations. Addition of Ni on the B2 TiPt phase resulted in the C′ values increasing and becoming positive at 31.25 and 43.75 at.% Ni respectively. Iridium addition increased the martensitic transformation temperature of the B2 – B19 (TiPt) phase with the lowest C′ shear modulus at 43.75 at.% Ir. However the addition of 43.75 at.% Pd decreased the transformation temperature of the B2 to B19 TiPt, as the shear modulus value C′ was -14 GPa.

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