Density functional theory study of TiPd alloying with Os as potential high temperature shape memory alloys

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Abstract. Ti₅₀Pd₅₀ alloy exhibits thermoelastic martensitic phase transformation above 823 K and has the potential for high temperature shape memory material applications. Previous studies showed that this alloy is mechanically unstable with a negative C' at room temperature. A systematic investigation of the structural, thermodynamic, electronic and elastic properties of TiPdOs is conducted using a first-principles calculation based on density functional theory. The calculated heats of formation show that this compound is thermodynamically stable as Os content is increased. It is found that an increase in Os content stabilizes the TiPd with a positive C' observed above 18.25 at. %. An increase in Os content results in an increase of the Bulk modulus and Young's modulus above 18.25 at. %. Anisotropy factor and Vickers hardness are studied and hardness is found to increase with an increase in Os content. The results suggest that the stability of the B2 phase can be significantly enhanced by the addition of Os in TiPd alloy. These findings have important applications for future materials design in aerospace industries.

1. Introduction
Shape memory alloys (SMAs) have the ability to remember their shape after being deformed and play an important role in many industries such as automotive, aerospace and medical. SMAs have drawn attention in commercial applications, due to their shape memory effects (SMEs) and superelasticity; this commercial development has been supported by research studies [1]. Amongst the SMAs, the Ti-Ni has been studied for a long period and is useful because of their unique sufficient ductility and shape memory properties [2]. However, these alloys have limited temperature around 373 K, so their applications are limited. Other SMAs such as Cu-Zn and Cu-Al alloys are also of commercial importance because of their low price, but they suffer instability of the martensitic phase and brittleness [3]. Recently, SMAs are being developed to suit many applications in many fields, especially for engineering properties. For example, TiNi-X SMAs (X=Pt, Pd, Hf, and Zr) have been considered for high temperature [4, 5]. However, their transformation temperature of remained below 830 K. Currently, the new SMA systems have been established in aerospace industry which can be alternative systems to TiNi include TiPd and TiPt as TiPd undertakes a B2-to-martensite phase transformation with Ms between 783 and 836 K. TiPd is well known as high temperature shape memory alloy (HTSMA) that can be used in engineering and medical industry due to the shape memory effect and superelasticity. This alloy has extraordinary mechanical behaviour and biocompatibility at 823 K [6]. TiPd HTSMA undertakes martensitic
transformation temperature (MTT) from the parent B2 (cubic) high temperature phase to the product B19 (orthorhombic) low temperature phase [7]. However, TiPd displays very poor shape-memory behavior during transformation, which results in poor corrosion resistance [2, 8]. Hence, the binary TiPd alloy has no strength for the use in actuators and aeronautic industry and ternary alloys will need to be established to improve their properties [9]. To enhance the performance of TiPd SMA which includes hardening, forgeability, corrosion resistance, and thermal stability, ternary alloying has been suggested. Osmium is most often used as an alloying agent with other PGMs and found in electrical contacts, styluses and medical devices and in other applications that need great strength and stiffness [10]. The addition of Os may enhance the transformation temperature of TiPd to above 1000 K. In this paper, the structural, thermodynamic, electronic and mechanical properties of the Ti$_{50}$Pd$_{50}$-xOs$_{x}$ alloys are systematically studied by the first-principles approach based on density functional theory (DFT). We found that addition of Os on B2 TiPd resulted in thermodynamically, electronically and mechanically stable system. The calculated results provided useful and practical guidance for further experimental and theoretical investigations on the future ternary shape memory alloys.

2. Methodology
The theoretical calculations in this paper were achieved using the Vienna ab initio simulation package (VASP) code based on the density functional theory (DFT) [11, 12]. In this calculation, the exchange and correlation functional was defined by Perdew, Burke, and Ernzerhof (PBE) [13] version of the generalized gradient approximation (GGA) [14]. A cutoff energy of 500 eV was used to converge the total energy of the structures. A 12 × 12 × 12 k-point was used for TiPd unit cell and equivalent numbers of k-points were used for the supercell, this according to Monkhorst and Pack [15]. The calculations were carried out using a 2x2x2 supercell having total number of 16 atoms. The substitutional search tool in VASP was used to substitute Pd with Os which provided the most stable composition at the desired symmetry. The calculations were determined at room temperature. For all structures, the elastic constants were calculated for a small strain of 0.005.

3. Results and discussions
3.1. Structural and thermodynamic properties
DFT equilibrium properties were obtained by firstly optimizing the crystal structures of Ti$_{50}$Pd$_{50}$-xOs$_{x}$ where the initial atomic positions and lattice constants were fully relaxed. Figure 1 (a) shows the calculated equilibrium lattice parameter of B2 Ti$_{50}$Pd$_{50}$-xOs$_{x}$ alloys. It is noted that the lattice parameter of Ti$_{50}$Pd$_{50}$-Os$_{x}$ alloys decrease almost linearly as the Os content is increased. This trend is attributed to the fact that the atomic radius of Os is smaller than that of Pd. The stability of Ti$_{50}$Pd$_{50}$-xOs$_{x}$ is discussed through the predicted heats of formation (ΔHf) and can be approximated by:

$$\Delta H_f = E_C - \sum x_i E_i$$

where $E_C$ is the determined total energy of the system and $E_i$ is the determined total energy of element in the system. The lowest negative value of ΔHf indicate stability of the structure, otherwise a positive value implies instability.

From figure 1 (b), it can be noted that the heats of formation of Ti$_{50}$Pd$_{50}$-xOs$_{x}$ alloys are all negative, which indicates the great possibility of form these compounds in the experiment. From the DFT ternary results, heats of formation decrease with an increase in Os content indicating thermodynamic stability. The result of the heats of formation are plotted in figure 1 (b) for Ti$_{50}$Pd$_{50}$-xOs$_{x}$ alloys.
3.2. Density of states

Electronic structure calculations have been performed to investigate the stability of TiPd-Os alloys by observing the trend of the total density of states (tDOS) near the Fermi level with respect to the pseudogap. The stability of TiPd when Os is added can be thus attributed to the lower and flatter tDOS near the Fermi level. When the fermi level (E_f) falls on the pseudogap, the structure is said to be the most stable otherwise the least stable structure. Similar analysis has been used by R Mahlangu and D A Pankhurst previously to describe the electronic stability trend for structures [16, 17]. In figure 2, we plot the total DOS for B2 Ti_{50}Pd_{50-x}Os_x (0 ≤ x ≤ 50) alloys where the black line marks the Fermi line (E_f). The Ti_{50}Pd_{50} structure hits the top of the total DOS peak indicating instability system. So adding the element that decreases the number of electrons will stabilize the system [18], hence Os was added. The Os has shown to have fewer electrons than Pd. As the composition of Os is added, the pseudogap moves towards the E_f which may imply that the system becomes electronically stable above 18.75 at. %. It is clearly seen that at 50 at. % Os (Ti_{50}Os_{50}) the Fermi level coincides with the pseudogap. This is consistent with the fact that Os has fewer electrons compared to Pd. The stability trend according to the density of states agrees very well with the predicted heats of formation results.

Figure 2. Comparison of the total density of states for TiPdOs structure against Energy.
3.3. Elastic properties

The elastic constants of a solid are very important parameters for determining the mechanical stability of the compounds. For the cubic symmetry B2 crystal structure of Ti₉₀Pd₅₀₋ₓOsₓ, there are three independent elastic constants which are c₁₁, c₁₂ and c₄₄. The calculated elastic constants and Anisotropy of Ti₉₀Pd₅₀₋ₓOsₓ alloys are shown in figure 3. The mechanical stability condition for the cubic system as defined elsewhere [19] are given as follows:

\[
c_{44} > 0; c_{11} > c_{12} \text{ and } c_{11} + 2c_{12} > 0,
\]

where the shear modulus \( C' \) can be calculated as:

\[
C' = \frac{1}{2}(c_{11} - c_{12})
\]

whereas the anisotropy can be calculated as:

\[
A = \frac{c_{44}}{C'}
\]

In figure 3, the calculated elastic properties of the Ti₉₀Pd₅₀₋ₓOsₓ alloys (0 ≤ x ≤ 50) are shown. For the structure to be stable, the stability condition for a cubic system must be fulfilled. The positive \( C' (1/2(c_{11} - c_{12}) > 0) \) indicates the mechanical stability of the system, otherwise, unstable. The binary B2 TiPd alloy is mechanically unstable at 0 K due to negative \( C' (-5.37 \text{ GPa}) \). From figure 3 (a), it is observed that \( c_{11}, c_{12} \) and \( c_{44} \) are greater than zero in all-inclusive ranges of Ti₉₀Pd₅₀₋ₓOsₓ alloys (0 ≤ x ≤ 50). At small Os content (below 6.25 at. % Os), the \( C' \) is negative suggesting that the structure is elastically unstable at this concentration. The shear modulus \( (C') \) is positive above 18.75 at. % Os which indicates the structures are mechanically stable. It is very important to study elastic anisotropy to understand material properties and improve their mechanical strength. When \( A = 1 \), the crystal is isotropic otherwise show elastic anisotropy \( (A \neq 1) \). The results showed that the elastic anisotropy values are smaller below 25 at. % Os and larger than the unity above. Anisotropy \( (A) \) becomes negative below 6.25 at. % which suggests that the material is anisotropic (figure 3 (b)). The calculated \( A \) for 43.75 at. % Os is close to the unit \( (A = 1) \) which indicates that the material is isotropic. Furthermore, the calculated \( A \) can be used to check the ductility in metals and the ratio should be greater than 0.8 [20]. The anisotropy is calculated and the values are greater than 0.8 above 18.75 at. % Os which reveal ductility behavior. Interestingly, an anisotropy ratio \( (A) \) is also of importance for determining the martensitic transformation of the material. A higher value of \( A \) indicates martensitic transformation from B2 to B19 while smaller \( A \) implies a good correlation between \( c_{44} \) and \( C' \) while leading to the transformation from B2 to B19′ [21]. As the composition of 18.75 at. % Os is added to the system, \( A \) is higher which confirms the transformation from B2 to B19. There is a strong coupling observed between the \( c_{44} \) and \( C' \) at 43.75 at. % Os which resulted in smaller anisotropy leading to transformation from B19 to B19′. It can be concluded that Ti₉₀Pd₅₀₋ₓOsₓ alloys undergo transformation from B2 to B19 martensite and then B19 transforms into B19′ due to a coupling of the \( c_{44} \) and \( C' \) at room temperature.
The elastic properties (GPa) of Ti\textsubscript{50}Pd\textsubscript{50-x}Os\textsubscript{x} SMAs.

Figure 3(b). The calculated anisotropy of Ti\textsubscript{50}Pd\textsubscript{50-x}Os\textsubscript{x} SMAs (0 \leq x \leq 50).

The calculated Bulk (B), Shear (G) and Young’s moduli for Ti\textsubscript{50}Pd\textsubscript{50-x}Os\textsubscript{x} alloys are shown in Figure 4. Mostly, the Bulk modulus is a degree of the hardness in materials. The calculated Bulk modulus increase with an increase in Os content, indicating that the material becomes harder at high content of Os. At 6.25 at. % Os, the structure appears to be more compressible and easily breakable as revealed by its relatively low negative moduli. The Shear modulus becomes positive and increases above 18 at. % Os, showing less compressibility. The calculated Young’s modulus can approximate the stiffness and the largest value relates to the stiffer material. The findings propose that Ti\textsubscript{50}Pd\textsubscript{6.25}Os\textsubscript{43.75} is the stiffest with the highest value of Young’s modulus.

Figure 4. Simulated elastic moduli B, G and E (GPa) for B2 Ti\textsubscript{50}Pd\textsubscript{50-x}Os\textsubscript{x} SMAs.

Figure 5 shows the calculated B/G ratio, Cauchy pressure, Poisson’s ratio and Vickers hardness (H\textsubscript{v}) at different compositions to assess the ductility/brittleness of the Ti\textsubscript{50}Pd\textsubscript{50-x}Os\textsubscript{x} alloys. The ratio of Bulk to Shear modulus was calculated as suggested by Pugh which predicts ductile/brittle behavior of the materials [22]. The highest value (B/G > 1.75) is related with ductility while low value (B/G < 1.75) relates brittleness. The values of B/G are lower than 1.75 at 6.25 at. % Os and higher above. The results
suggest that 18.75 at. % Os is more ductile with the highest value of 5.75 and more brittle at 6.25 at. % Os with the lowest value of -3.13 (see figure 5 (a)). This result further proves the same deduction with the anisotropy ratio which indicates a good correlation between B/G and anisotropy. Metals with a Poisson’s ratio greater than 0.26 are ductile otherwise brittle [23]. The results showed that all compositions are greater than 0.26 which indicates ductile behavior (see figure 5 (b)). For cubic crystal, the Cauchy pressure is well-defined as (c_{12}-c_{44}) for (100) plane. As suggested by Pettifor [24], the material with positive Cauchy pressure reveal their metallic bond character and ductile behaviour while a negative value indicates a weak covalent bond and exhibits brittle behaviour. The calculated Cauchy pressure is positive below 31.25 at. % Os which reveals their ionic character and ductile behaviour while above is negative indicating their weak covalent character and brittle behaviour (see figure 5 (c)). The Vickers hardness (H_V) of Ti_{50}Pd_{50-x}Os_{x} alloys are also calculated and are shown in figure 5 (d). It was found that the H_V increases as the concentration of Os are increased. This trend indicates that the hardest material can be obtained at the high content of Os, for example, Ti_{50}Pd_{62.5}Os_{37.5} with the hardness of 12.49.

![Figure 5. (a) The B/G ratio, (b) Poisson’s ratio, (c) Cauchy pressure (c_{12}-c_{44}) and (d) Vickers Hardness (H_V) for B2 Ti_{50}Pd_{50-x}Os_{x} SMAs.](image)

4. Conclusion
Using the DFT approach, we studied the lattice parameters, heats of formation, electronic structure and elastic properties of Ti_{50}Pd_{50-x}Os_{x} for potential HTSMAs. The results suggest that Ti_{50}Pd_{50-x}Os_{x} is thermodynamically stable with the lowest value of the heats of formation. It was found that Ti_{50}Pd_{50-x}Os_{x} alloys are mechanically stable above 18.75 at. % Os according to the criteria of mechanical stability. The ductile nature of Ti_{50}Pd_{50-x}Os_{x} alloys was confirmed from the value of the B/G ratio, Poisson’s ratio, Cauchy pressure (c_{12}-c_{44}) and anisotropy. Increasing Os above 6.25 at. % could effectively improve the ductility of the compound. The Bulk modulus (B), Shear modulus (G), Young’s modulus (E), and Vickers hardness (H_V), for the Ti_{50}Pd_{50-x}Os_{x} alloys, showed an increase tendency with an increase in Os.
content. The current findings and analysis may provide helpful direction for future design of new Ti₅₀Pd₅₀₋ₓOsₓ for potential high temperature applications.

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