Computational study of binary titanium-based potential shape memory alloys

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Abstract: First-principles density functional theory approach was employed to investigate the martensitic temperature of the equiatomic TiPt, TiZr and TiTa shape memory alloys. Firstly, their structural, thermodynamic, elastic and phonon dispersion have been deduced to mimic the relative stabilities. These alloys have potential to operate as high-temperature shape memory alloys since they possess a reversible B2 to B19 martensitic transformation. It was found that the lattice parameters are in good agreement with the experimental results to within 5%. Furthermore, the TiPt structure is thermodynamically stable displaying lowest heats of formation, while TiZr and TiTa are not. Our results show that the B2 phases of these binary alloys are vibrational unstable due to the presence of soft modes along high symmetry direction on the phonon dispersion curves. TiTa alloy is mechanically stable (C’ > 0), which may be used to develop future high-temperature alloys.

1. Introduction
Shape memory alloys (SMAs) are classified as a group of metals that can recall their pre-deformed shape upon temperature increase and this is due to their two unique properties, shape memory effect (SME) and superelasticity [1]. These materials exhibit martensitic transformation between high-temperature austenite (B2) to low-temperature martensite phases (B19/19′) [2]. Ti-based SMAs have been used for various applications in the medical and engineering industry [3, 4]. Amongst the binary alloys, TiNi is the most studied and commercialized SMA, but its applications are limited by low martensitic transformation temperatures (Tm) of 373 K [5]. Thus, the development of SMAs that can operate at high temperature is ongoing, in particular to increase the application areas and shape memory properties [6]. Ti-based SMAs such as TiPd, TiTa and TiPt have been studied in the experimental and theoretical researches owing to their high transformation temperature which render them appropriate for potential high-temperature applications [7]. Amongst these alloys, TiTa was found attractive for advanced actuators applications due to their shape memory behaviour at relatively high temperatures [8]. Furthermore, TiPt is the most attractive for the development of high-temperature shape memory alloys (HTSMAs) since it has high Tm of about 1300 K [9]. This alloy has been reported to undergo a reversible martensitic transformation from B2 to B19/B19′ at this temperature.
Recently, many theoretical and experimental studies are being carried to explore the SMAs properties, particularly features pertaining transformation temperature and stability; this phenomenon is still not well understood [10]. In this paper, we investigate the stability of TiM (M = Pt, Ta, Zr) SMAs at 50:50 composition using the heats of formation, elastic properties and phonon dispersion curves of B2 structures. It was found that TiPt and TiZr structures are unstable at 0K, in agreement with experimental findings [10, 11]. Our results also showed that all the B2 structures are vibrational unstable displaying since soft modes are observed along high symmetry direction in the phonon spectra. However, TiTa has shown potential for new alloy development, being elastically stable at 0K.

2. Methodology
First-principles density functional theory (DFT) [12] approach with the projector augmented wave [13] was employed to investigate the stability of the equiatomic titanium-based SMAs using VASP code [14]. An energy cutoff of 500 eV was used, as it was adequate to converge the total energy of the systems. For exchange-correlation functional, the generalized gradient approximation of Perdew, Burke and Enzerhof (GGA-PBE) [15] was chosen. The suitable k-points mesh according to Monkhorst and Parck [16] of 8×8×8 was used. 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. Structural properties
The calculated equilibrium lattice parameters and heats of formation of B2 Ti-M (M=Pt, Ta, Zr) alloys are shown in Table 1. It is found reasonable that equilibrium lattice parameters are in good agreement with experimental to within 5%. TiPt lattice parameter is 3.179 Å compared to 3.192 Å [18]. In addition, TiZr lattice parameter agrees with a value of 3.418 Å (3.040) [19], while TiTa is well predicted as 3.269 Å (3.350) [20].

The heat of formation is used to predict the stability of alloys and may be calculated as,

$$\Delta H_f = E^{TiPt} - [(1-x)E^{Ti}_{solid} + xE^{Pt}_{solid}],$$

where $E^{TiPt}$, $E^{Ti}_{solid}$ and $E^{Pt}_{solid}$ are the total energies of an intermetallic alloy, and elemental Ti and Pt in their respective ground-state crystal structures, while x and 1-x refer to the fractional concentrations of the constituent elements. The lowest heats of formation value indicate stability whereas highest indicates instability of the material. It is clear that TiPt is found to be more stable with the lower heats of formation of -0.821 eV/atom while that of TiZr and TiTa were found to be the least stable with the highest heats of formation of 0.065 eV/atom and 0.005 eV/atom, respectively.

Table 1. Equilibrium lattice parameters (a) and heats of formation (ΔHf) of B2 Ti-M (M=Pt, Zr, Ta) binary alloys.

| Structures | a (Å)       | Calculated | Experimental | ΔHf (eV/atom) |
|------------|-------------|------------|--------------|---------------|
| TiPt       | 3.179       | 3.192 [18] |              | -0.861        |
| TiZr       | 3.418       | 3.040 [19] |              | 0.065         |
| TiTa       | 3.269       | 3.350 [20] |              | 0.005         |

3.2. Elastic constants
The elastic constants ($C_{ij}$), anisotropy (A) and Pugh’s ratio (B/G) of Ti-M (M=Pt, Zr, Ta) alloys were calculated as shown in Table 2. The elastic properties investigation is considered in this study to understand martensitic transformation behaviour of these alloys [11]. There are three independent elastic constants ($C_{11}$, $C_{12}$ and $C_{44}$) for a cubic crystal structure, shear modulus $C’$ and A to evaluate the stability and transformation behaviour. In order to gain a deep understanding of the mechanical durability of these alloys, we calculated the anisotropic factor A,

$$A = \frac{C_{44}}{C’}. \quad (2)$$

The stability criterion for the cubic system are as follows;

$$C_{44} > 0, \quad C_{11} + 2C_{12} > 0, \quad \text{and} \quad C_{11} > |C_{12}|. \quad (3)$$

Note that the crystal structure is considered to be mechanically stable when $C’$ is positive, otherwise unstable. In this case, the calculated elastic constant show that $C_{11} < C_{12}$ for a cubic TiPt and TiZr structures leading to negative shear modulus $C’$ ($C’ < 0$). This indicates that the structures are mechanically unstable. It was reported that cubic TiPt is unstable at low temperature with $C’$ of -32 GPa. Our calculated elastic constants values are all positive, it is an indication of mechanical stability of a cubic TiTa at low temperature. In addition, the lower shear modulus $C’$ of TiZr (-25.49 GPa) suggesting the higher B19 transformation temperature. Higher A is necessary for B2-B19 phase transformation. Thus, there is a stronger correlation between $C_{44}$ and shear modulus $C’$ of TiTa and is considered anisotropic (A≈1). Calculated A is smaller with value of 0.95 suggesting the B2 to B19’ phase transformation. To investigate the ductility of these alloys, bulk (B) and shear (G) moduli are considered. The Pugh’s ratio clearly indicates that all binaries in this study are ductile with B/G>1.75 [21].

| Structures   | $C_{11}$ (GPa) | $C_{12}$ | $C_{44}$ | $C’$  | $C$  | A   | B/G |
|--------------|----------------|----------|----------|-------|------|-----|-----|
| TiPt [7]     | 145            | 210      | 45       | -32   | -    | 2.28|     |
| TiZr         | 59.90          | 110.88   | 17.74    | -25.49| -    | 3.38|     |
| TiTa         | 204.25         | 121.26   | 39.46    | 41.50 | -    | 0.95| 3.70|

3.3. Phonon dispersion

Phonon dispersion and phonon density of states (DOS) were also calculated to investigate the vibrational properties of TiM (M=Pt, Zr, Ta) and are displayed in figure 3. There are soft modes observed on the curves signifying the instability of the phases with reverence to the vibrations of the atoms. TiPt, TiZr and TiTa are vibrational unstable due to the existence of soft modes observed in the negative frequency. In particular, along the M and R high symmetry directions and this could be attributed to high vibration of Pt atoms in the TiPt, Zr atoms in TiZr and Ta atoms in TiTa as depicted on the phonon DOS. The phonon dispersion curves of the binary B2 phase for TiPt and TiZr are mostly characterized by the negative value of shear modulus $C’$ which is related to elastic behaviour. These soft modes have the lower frequency at approximately -3.0 THz due to high vibration of Pt, Ta and Zr atoms.
Figure 1. Phonon dispersion curves of (a) TiPt, (b) TiTa and (c) TiZr binary alloys.

4. Conclusion
Our DFT results displayed reasonable structural properties, elastic properties and phonon dispersion of TiM (M=Pt, Zr, Ta) alloys. The calculated equilibrium lattice parameters are in accord with the experimental findings to within 5%. It is interesting to note that the predicted heats of formation confirmed the stability of TiPt. However, Pugh’s ratio clearly indicates that all the structures in this study are ductile. Elastic constants show that TiTa is mechanically stable satisfying the cubic stability criterion. Furthermore, phonon dispersion spectra showed that TiPt and TiZr are vibrationally unstable, due to the presence of soft modes observed along high symmetry directions in the Brillouin zone , which is in agreement with the predicted elastic constants.
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