The effects of Ru, Cu, Zr and Hf on mechanical properties in Ti-Pt high temperature shape memory alloys

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Abstract. Shape memory alloys (SMAs) have been widely used in the fields of actuators and aerospace industry due to their pseudo-elasticity and shape memory effect which are displayed in phase transformations. The martensitic transformations (MT) of TiPt is much higher, at approximately 1273 K and this is considered to be of potential technological interest for elevated temperature SMA applications. TiPt based alloys exhibit very low shape memory effect due to low critical stress for slip deformation compared to the stress required for martensitic transformation, hence it is necessary to enhance the mechanical properties of the equiatomic alloy. The first principles approach was employed to study the effect of the third element (M = Ru, Cu, Zr, and Hf) on the TiPt shape memory alloy. The supercell approach in VASP was used to substitute Pt with Ru and Cu, Ti with Zr and Hf on the TiPt structure to evaluate their mechanical stability from elastic properties for actuators and higher temperature applications. The Ti50Pt50,Ru, and Ti50Pt50,Cu, decreases in density with increase in Ru and Cu concentration, whilst the Ti50,Zr,Pt50 and Ti50,Hf,Pt50 substitution increases with an increase in their concentration, which result in larger lattice parameters. The heats of formation suggest that Ti50,Pt50,Ru, substitution is more thermodynamically stable than Ti50,Pt50,Cu, substitution, and Ti50,Hf,Pt50 substitution is more stable than Ti50,Zr,Pt50. The elastic properties suggest that the ternary structures become mechanically stable with an increase of the third element. The Ti50,Pt50,Ru, and Ti50,Pt50,Cu, substitution became more ductile with the increase in concentration. Zr and Hf substitution became more ductile at higher compositions (31.75 – 43.75 at.%). The Ru and Hf substitutions have potential to be used for high-temperature applications.

1. Introduction
Shape memory amalgams (SMAs) that display shape memory impact over 373 K can possibly be utilized for higher temperature application, for example, air ship turbine motors, high-temperature actuators, thermal security, and so forth. [1]; these are known as high-temperature shape memory alloys (HTSMAs). Of all the known SMA pieces, the NiTi compound framework has been examined most broadly and is utilized in the best number of business applications. This alloy exhibits strong shape memory effect (SME), and pseudoelastic behavior under the right conditions, which makes this material ideal for a variety of applications [2]. HTSMAs are produced by adding the ternary (third elements) such as Pd, Pt, Hf, Au, and Zr to NiTi for whose temperature can be shifted anywhere between 373 and 973 K [3]. Some of these materials were reported to effectively increase the transformation temperature of NiTi [4]. Hafnium and Zr addition to NiTi has also been investigated due to their lower cost [5].
+ Hf, Zr) - rich NiTi amalgams have weaknesses, for example, an enormous warm hysteresis, poor thermal steadiness, and fragility [6].

On the other hand, equiatomic TiPt exhibits martensitic phase transformation above 1200 K, ~400K higher than equiatomic TiAu and ~500K higher than equiatomic TiPd [7, 8]; these are categorized as HTSMAs due to their thermo-elastic B2 martensitic phase transformation to B19 above 700 K [1, 9, 10]. It was also found that TiPt alloys exhibited negligible SME (11%), due to the low critical stress for slip deformation compared to the stress required for martensitic reorientation [11]. Yoko Yamabe-Mitarai and co-workers [12] additionally detailed that Ti – 50Pt displayed a solitary yielding marvel and low quality (~450MPa) in martensite and exceptionally low quality (~20 MPa) in the B2 area.

Equiatomic Equiatomic TiPt displayed thermo-flexible martensitic phase change, and may not be utilized for high-temperature shape memory materials applications, because of irrelevant SME and low reinforcing in the austenite region. Otherwise, if the shape memory properties can be improved, the B2 phase could be utilized for higher temperature applications [13, 14]. However, research on TiPt enhancement with Zr and Ru partial substitution were discovered powerful for improving the high-temperature quality and shape memory properties, bringing about an expansion in critical stress for slip disfigurement [14]. Cobalt addition was reported to stabilize the B2 phase at lower temperatures and reduced the martensitic transformation temperature due to higher values of tetragonal shear modulus (C') [15].

Furthermore, it is important to strengthen both martensite and austenite phase against deformation, which is significant for the development of SMAs for high-temperature actuator applications [16]. In the previous work, the effect of a third element Ru, Co, Cu, Zr and Hf on the B19 Ti50Pt50, was investigated for x=5 and Ru addition was more effective and preferred for high-temperature shape memory alloys [17]. It has been suggested that Ru and Cu are preferential for Pt substitution, while Zr and Hf showed promising shape memory trends when substituted for Ti site [18]. In this study we investigated the thermodynamic and elastic properties of the B2 ternary Ti50Pt50, M=Ru and Cu and Ti50,M,Pt50 =Zr and Hf shape memory alloys by employing the first principles method for understanding their martensitic transformation behavior and mechanical properties.

2. Methodology

We employed the first principles density functional theory (DFT) in the Vienna *ab initio* Simulation Package (VASP) code [19, 20] with the projector augmented wave (PAW) [21]. An energy cut–off of 500 eV was used, to achieve a good convergence of the parameters. We used the generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional [22]. The Brillouin zone integrations were performed with a k-spacing of 0.25 according to Monkhorst and Pack [23]. A 2x2x2 supercell of TiPt was used to substitute a portion of the Pt with Ru and Cu, and Ti with Zr and Hf.

3. Results and Discussion

3.1. Structural and Thermodynamic Properties

The calculated equilibrium lattice parameters of the B2 Ti50Pt50,M, where M=Ru and Cu are shown in Figure 1 (a), B2 Ti50,M,Pt50 =Zr and Hf in Figure 1 (b) (x=6.25, 18.75, 25, 31.75, and 43.75), where a = b = c. The lattice parameters decreased with increased Ru and Cu content with Ti50Pt6.25Ru43.75 having the lowest value of lattice parameter at a=3.085 Å. Conversely, Ti50,Zr,Pt50 and Ti50,Hf,Pt50 substitutions increased with an increase in Zr and Hf content, Ti43.75Hf6.25Pt50 being the lowest at a=3.304 Å.

Figure 1 (c) and (d) show the densities of Ti50Pt50,M, where M=Ru and Cu and Ti50,M,Pt50 =M=Zr and Hf against composition. The density of the Ti50,Pt50,Ru, and Ti50,Pt50,Cu, substitutions decreased with increase in Ru and Cu content, which was also verified by the lattice parameters, this might be due to their atomic radius of Ru and Cu being less than that of Pt. So partial substitution of Pt on Ti50,Pt50,M, with Ru was expected to decrease the density of the TiPt alloy [24]. Ti50Pt6.25Cu43.75 was found to have
the lowest density. On the contrary, Ti$_{50}$Hf$_{50}$Pt$_{50}$ increased as 43.75$>x>6.25$, Ti$_{50}$Zr$_{50}$Pt$_{50}$ was observed with a minimal increase with an increased Zr composition. It can also be seen that the atomic radii of Zr and Hf are much greater than both Ti and Pt, resulting in greater densities on the ternary alloys.

![Figure 1](image)

Figure 1. Equilibrium lattice parameters of (a) Ti$_{50}$Pt$_{50}$M$_{x}$ (M=Ru and Cu) (b) Ti$_{50}$M$_{x}$Pt$_{50}$ (M=Zr and Hf) and densities of (c) Ti$_{50}$Pt$_{50}$M$_{x}$ (M=Ru and Cu) (d) Ti$_{50}$M$_{x}$Pt$_{50}$ (M=Zr and Hf) ternaries, 43.75$>x>6.25$.

The heats of formation ($\Delta H_f$), of the intermetallic phase were calculated according to the relation [25]:

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

(1)

where $E^{TiPt}$, $E^{Ti}_{solid}$ and $E^{Pt}_{solid}$ are the total energies of an intermetallic compound, and basic Ti and Pt in their particular ground-state crystal structures, while x and I-x allude to the fragmentary convergences of the constituent components.

The predicted heats of formation for Ti$_{50}$Pt$_{50}$M$_{x}$, where M=Ru and Cu and Ti$_{50}$M$_{x}$Pt$_{50}$ M=Zr and Hf are shown in Figure 2. The heats of formation suggest that the small composition of Ti$_{50}$Pt$_{43.75}$Ru$_{6.25}$ (~0.748 eV/atom) and Ti$_{50}$Pt$_{43.75}$Cu$_{6.25}$ (~0.693 eV/atom) are more stable; as the Cu content is increased the Ti$_{50}$Pt$_{50}$Cu$_{x}$ became unstable. Ru is more stable than Cu substitution on Ti$_{50}$Pt$_{50}$M$_{x}$. On the contrary, Ti$_{6.25}$Zr$_{43.75}$Pt$_{50}$ (~0.908 eV/atom) and Ti$_{6.25}$Hf$_{43.75}$Pt$_{50}$ (~0.966 eV/atom) suggest that they are more stable substitutions. Ti$_{50}$Zr$_{50}$Pt$_{50}$ and Ti$_{50}$Hf$_{50}$Pt$_{50}$ became more stable when their concentration was increased and Hf substitution became more stable.
3.2. Elastic Properties

The accurate calculation of elasticity is vital for picking up knowledge into the mechanical stability and elastic properties of compounds. The elastic constants of a cubic crystal have three \( (C_{11}, C_{22}, \text{and } C_{44}) \) independent elastic constants. Applying two sorts of strains \( (\varepsilon_1 \text{ and } \varepsilon_4) \) on the cubic system give stresses identifying with three flexible coefficients, yielding a proficient technique for obtaining elastic constants. This technique has been effectively used to study the elastic properties of a scope of materials including metallic frameworks [26].

For a cubic crystal, the mechanical stability conditions are given by [27].

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

(2)

The elastic constants were evaluated to observe the impact of ternary substitution Pt with Ru and Cu, and Ti with Zr and Hf. All the independent elastic constants \( C_{11}, C_{12}, \text{and } C_{44} \) for \( Ti_{50}Pt_{50-x}M_x \) where \( M=\text{Ru and Cu} \) and \( Ti_{50}Pt_{50-x}M_{x} \text{, where } M=\text{Zr and Hf} \) were positive which indicated mechanical stability of the structures. The \( C_{11} > C_{12} \) at 25 at.% and 43.75 at.% for \( Ti_{50}Pt_{50-x}Ru_\text{Ti} \) in Figure 3 (a), \( C_{11} > C_{12} \) at 18.75–43.75 at.% for \( Ti_{50}Pt_{50-x}Cu_\text{Ti} \) in Figure 3 (b), \( C_{11} > C_{12} \) at 18.25–43.75 at.% for \( Ti_{50}Pt_{50-x}Zr_\text{Ti} \) in Figure 3 (c), and \( C_{11} > C_{12} \) at 25–43.75 at.% for \( Ti_{50}Pt_{50-x}Hf_\text{Ti} \) in figure 3 (d), which contributed to positive \( C' \). However, the \( C_{44} \) increase minimally with increase in \( Ti_{50}Pt_{50-x}Ru_\text{Ti} \) and \( Ti_{50}Pt_{50-x}Cu_\text{Ti} \) substitutions, suggesting a good correlation between \( C_{44} \) and \( C' \) moduli, while decreasing minimally for \( Ti_{50}Pt_{50-x}Zr_\text{Ti} \) and \( Hf_\text{Ti} \) substitution. The positive shear suggests that all the ternary compositions above satisfied all conditions of mechanical stability of the cubic crystal.
The Ru and Cu substitution became mechanically stable with an increase in content, 25 – 43.75 at.% Ru and Cu from 18.75 at.% as shown in Figure 4 (a), Zirconium substitution stabilizes around 43.75 at.%, whilst Hf from 25 at.% in Figure 4 (b). The C’ increases with increase in Ru, Cu, Zr, and Hf content, it is also observed that smaller C’ values lead to larger anisotropy (A). These suggest that the Group 4 substitution stabilizes with an increase in Zr and Hf content, Ru belongs to Group 8, a similar trend was observed with the heats of formation; this might be due to Ru having a lower atomic radius than both Ti and Pt. Ti50Pt50-Cu in Figure 4 (a) stabilized around 18.75 at.% and it also noted that Cu has an atomic radius less than that of Pt, hence the observed curve.

Furthermore, Ru substitution reduced the martensitic transformation temperature of TiPt [14] more than Ti50Pt6.25Cu43.75, indicated by higher C’, which is consistent with the experimental findings at lower concentrations for Ru substitution. The C’ moduli of Ti50Pt6.25Ru43.75 correspond with A of 0.78, closer to unity (A=1) [28]. The Hf substitution in Figure 4 (b) increased the martensitic transformation temperature of the Ti50Pt50 since it gave the lowest C’ at 6.25 at.%, with an A value of 0.87. The Bulk modulus (B) measures the level of firmness, or the energy required to deliver a given volume disfigurement [29]. In Figure 4 (c), Bulk moduli for Ti50Pt50-Ru increased with an increase in Ru content, suggesting that the structure became more hardened, while Ti50Pt50-Cu decreased with increased Cu content, suggesting that it became less hardened. Ti50-Zr50, Pt50 and Ti50,Hf50 in Figure 4 (d) both decreased with increase in Zr and Hf content. These suggest that to maintain the hardness of Ti50Pt50-Ru, can be used with higher substitutional content, while Ti50Pt50,Cu, Ti50,Zr,Pt50, and Ti50,Hf,Pt50 may have to be used at smaller substitutional content.

Figure 3. Independent elastic properties $C_{ij}$ ($C_{11}$, $C_{12}$, and $C_{44}$) (GPa) of (a) Ti50Pt50-xRu$_x$ (b) Ti50Pt50-xCu$_x$ (c) Ti50-xZr$_x$Pt50 (d) Ti50-xHf$_x$Pt50, where 43.75>$x$>6.25
Cu in demonstrates Ru having a place with Group 8 of the Periodic Table go about as B2 phase stabilizer to a positive anisotropy. The substitutions were found to be stable with all the moduli obeying the elastic stability criterion. The elastic constant of both for Pt and Hf, we observed that Ru and Cu showed a decrease in lattice parameter, while Zr and Hf show an increase. The thermodynamic stability for the ternary framework was explored by substituting a portion of the Pt with Ru and Cu, and Ti with Zr and Hf, we observed that Ru (−0.748 eV/atom) at 6.25 at.% and Hf (−0.966 eV/atom) at 43.75 at.% substitutions were the most stable structures. The elastic constant of both for Pt substitution and Ti substitution were found to be stable with all the moduli obeying the elastic stability criterion. The addition of Ru and Cu content in Pt and Zr and Hf in Ti increased C’ moduli of the cubic phase leading to a positive anisotropy. Ti₅₀Pt₅₀ₓRuₓ and Ti₅₀Pt₅₀ₓHfₓ where 0<x<50 was performed. The effect of the lattice parameter depends on the type of the alloying element and sub-lattice. The Ru and Cu showed a decrease in lattice parameter, while Zr and Hf show an increase. The thermodynamic stability for the ternary framework was explored by substituting a portion of the Pt with Ru and Cu, and Ti with Zr and Hf, we observed that Ru (−0.748 eV/atom) at 6.25 at.% and Hf (−0.966 eV/atom) at 43.75 at.% substitutions were the most stable structures. The elastic constant of both for Pt substitution and Ti substitution were found to be stable with all the moduli obeying the elastic stability criterion. The addition of Ru and Cu content in Pt and Zr and Hf in Ti increased C’ moduli of the cubic phase leading to a positive anisotropy. Ti₅₀Pt₅₀ₓRuₓ and Ti₅₀Pt₅₀ₓHfₓ increases the transformation temperature. This demonstrated Ru having a place with Group 8 of the Periodic Table go about as B2 phase stabilizer than Cu in Pt substitution, followed by Hf in Ti substitution.

4. Conclusions
A computational modelling study on the thermodynamic and mechanical properties in Ti₅₀Pt₅₀ₓMₓ (M=Ru and Cu) and Ti₅₀ₓM₅₀Pt₅₀ (M=Zr and Hf) where 0<x<50 was performed. The effect of the lattice parameter depends on the type of the alloying element and sub-lattice. The Ru and Cu showed a decrease in lattice parameter, while Zr and Hf show an increase. The thermodynamic stability for the ternary framework was explored by substituting a portion of the Pt with Ru and Cu, and Ti with Zr and Hf, we observed that Ru (−0.748 eV/atom) at 6.25 at.% and Hf (−0.966 eV/atom) at 43.75 at.% substitutions were the most stable structures. The elastic constant of both for Pt substitution and Ti substitution were found to be stable with all the moduli obeying the elastic stability criterion. The addition of Ru and Cu content in Pt and Zr and Hf in Ti increased C’ moduli of the cubic phase leading to a positive anisotropy. Ti₅₀Pt₅₀ₓRuₓ and Ti₅₀Pt₅₀ₓHfₓ increases the transformation temperature. This demonstrated Ru having a place with Group 8 of the Periodic Table go about as B2 phase stabilizer than Cu in Pt substitution, followed by Hf in Ti substitution.
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