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Mechanical properties and stability of TiPt-M (M= Ru, Co, Cu, Zr and Hf) for high temperature applications

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Abstract. Shape memory alloys are smart materials that can remember their shape after being deformed. This is due to their unique properties, shape memory effect and super-elasticity, which occurs because of phase transformation. High temperature shape memory alloys are being developed in order to increase the application area of shape memory alloys. There is an increasing demand of shape memory alloys, which can be used in high temperatures environments such as in aerospace, actuators, sensors in the automotive industry. The first-principle approach was employed to investigate the effect of ternary alloying with Ru, Co, Cu, Zr and Hf on the equi-atomic B19 TiPt alloy. The supercell approach based on the B19 TiPt structure was used to construct various compositions containing a third element with reduced Pt content, and evaluate their thermodynamic and mechanical stability. The Ru, Co and Cu calculations were performed to compare their effects on the TiPt relative to Zr and Hf addition. It was found that partial substitution with Ru was the most stable structure as compared to the Hf, since it displayed the lowest heats of formation. Their martensitic transformation temperature increased due to their lowest C′ shear modulus. However, the addition of Cu reduced the transformation temperature of the TiPt. All structures were found to be completely anisotropic.

1. Introduction

Shape memory alloys (SMAs) are used in a wide range of industrial applications, such as medical, actuators, robotics, energy and aerospace, due to their unique properties, shape memory effect (SME) and pseudo-elasticity which occurs as a result of phase transformation [1]. Recently, high temperature shape memory alloys (HTSMAs) have been investigated in order to increase the application areas of shape memory alloys. A number of alloying elements such as Pt, Pd, Hf and Zr have been studied in the attempt to increase the transformation temperature of NiTi (373 K). The NiTi-Pt and NiTi-Pd was reported to be effective in increasing the transformation temperature of the NiTi binary [2, 3]. However, the martensitic transformation temperature of these alloys remains below 830 K. TiPd and TiPt at equi-atomic have a high temperature phase identified as the cubic B2 austenite and low temperature phase as orthorhombic B19 martensite. They undergo phase transformation from B2 phase to B19 phase at 850 K and 1300 K [4]. TiPd have poor shape recovery of ~10% after deformation at 773 K, due to low strength at high temperature causing plastic deformation during stress application [5]. TiPt based alloys exhibit very low SME due to low critical stress for slip deformation compared to the stress required for martensitic transformation (MT) [6]. Interestingly the

alloys have the potential to be used for much higher-temperature shape memory applications due to their high martensitic transformation Tm if their shape memory properties can be enhanced [7, 8].

Numerous attempts to enhance the mechanical properties of TiPt have been reported by adding elements such as Ir, Co, Ru, Zr and Hf [9, 10]. The shape recovery ratio of TiPt-Ir remained lower around 10% [11, 12]. Co, Ru, Zr and Hf addition improved the shape recovery ratio to between 40% and 60% [13]. Among these alloying metals, Zr and Hf were found to be most effective to enhance the shape memory recovery ratio. In this work, density functional theory (DFT) based technique was used to study the effect of the third element Ru, Co, Cu, Zr and Hf on the B19 TiPt-M system (shown in Figure 1). The stabilities of the $Ti_{50}Pt_{50-x}M_x$ for x=5 were investigated by studying the heats of formation and elastic properties of the structures. The calculations revealed Ru is the most thermodynamically stable addition as compared to the other structures. It will be shown that the Ru addition is more preferential, to contribute as HTSMAs.

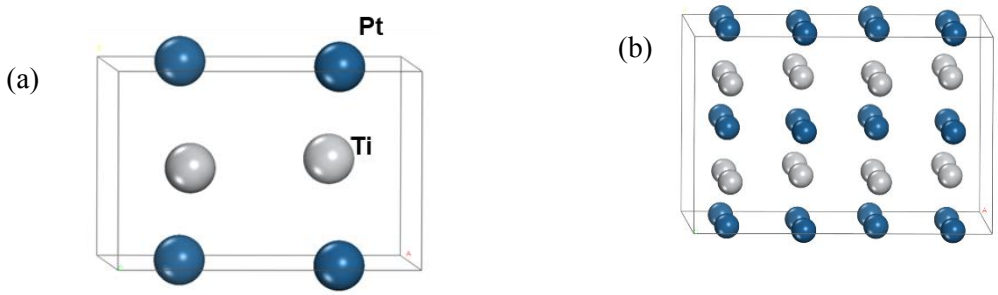

Figure 1. The atomic arrangement (a) Unit cell of B19 TiPt system with a space group Pmma. (b) Supercell for B19 TiPt-M structure.

2. Methodology

The calculations were carried out using the ab initio DFT in the Vienna ab initio Simulation Package (VASP) code [14, 15] with the projector augmented wave (PAW) [16]. An energy cutoff of 500 eV was used, to achieve a good convergence of the parameters. We have used the generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional [17]. The k-spacing of 0.18 for B19 TiPt was used according to Monkhorst and Pack [18].

3. Results and Discussion

3.1. Structural and Thermodynamic Properties

In Table1, the calculated equilibrium lattice parameters of the B19 $Ti_{50}Pt_{45}M_5$ are shown where M= Ru, Co, Cu, Zr, and Hf. The calculated results show that Ru, Co, and Cu decrease the equilibrium lattice parameter of the system, due to the atomic radii of Cu (135 pm) and Co (135 pm) being equal to that of Pt (135 pm), Ru being less than both Ti and Pt. The lattice parameters of both Zr and Hf increased minimally; this might be due to the larger atomic radii of Zr (155 pm) and Hf (155 pm) relative to Ti (140 pm) and Pt (135pm), respectively. Ru has a lower density of 12.37 g/cc than Pt (21.45 g/cc), the atomic radii of Ru is also lower (130 pm) than both Ti and Pt, but high in melting point of 2607 K. This attributed to Ru having lower lattice parameters. Similarly, the partial substitution of Co on Pt sub-lattice also reduced the lattice parameters of TiPt [19]. Therefore, the lattice parameter depends on the type of the alloying or third element [20]. The densities of both Zr and Hf are higher than that of Ti, which means that partial substitution of Ti with Zr or Hf will increase the density of the equi-atomic TiPt shape memory alloys.

Table 1. The equilibrium lattice parameters of B19 TiPt and $Ti_{50}Pt_{45}M_5$ (M= Ru, Co, Cu, Zr and Hf) ternaries.

Structures	$Ti_{50}Pt_{50}$	$Ti_{50}Pt_{45}M_5$ (M= Ru, Co, Cu, Zr and Hf)				
	-	Ru	Co	Cu	Zr	Hf
Lattice Parameters (Å)	a=4.618 (4.650) [4]	4.579	4.567	4.611	4.660	4.653
	b=2.857 (2.828)	2.805	2.778	2.768	2.817	2.819
	c=4.891 (4.940)	4.852	4.860	4.862	4.849	4.846
ΔH_f (eV/atom)	-0.932 (-0.962)	-0.864	-0.851	-0.834	-0.807	-0.804

The heats of formation (ΔH_f), of the intermetallic phase is calculated according to the relation [21],

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

where E^{TiPt}, E^{Ti}_{solid} and E^{Pt}_{solid} are the total energies of the alloy, elemental Ti and Pt in their respective ground-state crystal structure; respectively whereas *x* and *1-x* refers to the fractional concentrations of the constituent elements.

In Figure 2, we present plots of the predicted $Ti_{50}Pt_{45}M_5$ heats of formation for analysis. Ru substitution has the lowest value of heats of formation compared to Co and Cu dopants with Zr and Hf having the largest values. Co and Cu are more stable in comparison to Zr and Hf. Therefore, Ru is considered to be the most stable substitution with the value -0.8640 eV/atom.

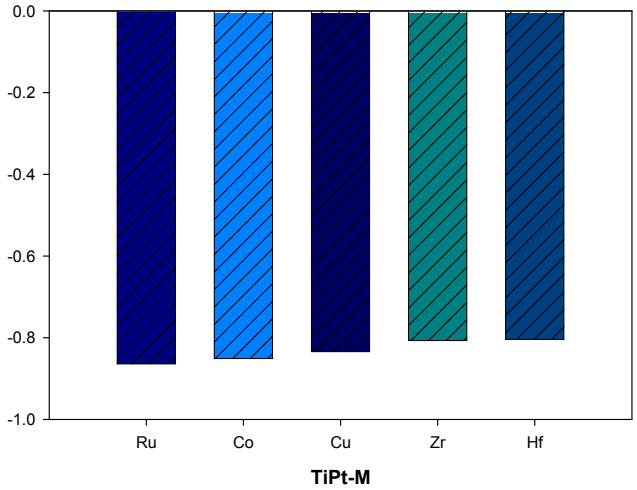

Figure 2. Heats of formation of $Ti_{50}Pt_{45}M_5$ (M= Ru, Co, Cu, Zr and Hf) alloys.

3.2. Elastic Properties

The accurate calculation of elasticity is crucial to gain insight into the mechanical stability and elastic properties of compounds. Their elastic constants depend on the type of lattice i.e for an orthorhombic crystals; there are nine (C_{11}, C_{22}, C_{33}, C_{12}, C_{13}, C_{23}, C_{44}, C_{55}, $C_{66,}$) independent elastic constants, respectively. This method has been successfully used to study the elastic properties of a range of materials including metallic systems [22].

For orthorhombic crystal, the mechanical stability conditions are given by [23].

$$C_{11} + C_{12} + C_{33} + 2C_{12} + 2C_{13} + 2C_{23} > 0,\ C_{22} + C_{33} - 2C_{13} > 0,\ C_{11} > 0,$$

$$C_{22} > 0,\ C_{33} > 0,\ C_{44} > 0,\ C_{55} > 0,\ C_{66} > 0. \quad (2)$$

The elastic constants and moduli for doped B19 $Ti_{50}Pt_{50-x}Mx$ structures are listed in Tables 3. The elastic constants were evaluated to observe the effect of ternary addition for Ru, Co, Cu, Zr and Hf concentrations of 5 atomic percent. The shear modulus (C′) for all the ternaries was positive, with Zr having the lowest value and Ru the largest, which translates to higher transformation temperature. The positive shear suggests that all the ternaries satisfy all conditions of mechanical stability of an orthorhombic crystal. Furthermore, anisotropic ratio (less micro cracks in the material), approaches unity (A=1) for all structures which indicates a strong correlation between C_{44} and C′ shown in figure 3. Considering that the shear modulus represent the resistance to plastic deformation and the bulk modulus represent the resistance to fracture [23], the Pugh ratio (B/G) was calculated and evaluated to determine the ductility and brittleness of the structures. The structures were observed to be ductile since all the structures were greater than the critical value of 1.75 [24]. The calculated young (E) moduli suggest that the Ru is least stiff material than Cu, which correlates greatly with C′ values. Therefore, Ru was found to be the most stable substitution.

Table 2. The elastic properties C_{ij} (GPa) of the $Ti_{50}Pt_{45}M_5$ (M= Ru, Co, Cu, Zr and Hf) ternaries and their anisotropy (A).

Elastic Constant C_{ij} (GPa)		$Ti_{50}Pt_{45}M_5$ (M= Ru, Co, Cu, Zr and Hf)				
	TiPt [8]	Ru	Co	Cu	Zr	Hf
C_{11}	319	322	312	312	289	290
C_{12}	133	138	143	135	133	130
C_{13}	152	153	145	139	138	137
C_{22}	361	346	356	357	322	306
C_{23}	112	115	109	112	105	104
C_{33}	317	310	309	315	296	297
C_{44}	-60	49	58	61	59	59
C_{55}	57	51	55	59	57	56
C_{66}	65	60	66	64	67	67
$C'=(C_{11}-C_{12})/2$	93	92	85	89	78	80
$A_1=2C_{66}/(C_{11}-C_{12})$	0.7	0.7	0.8	0.7	0.9	0.8
$A_2=2C_{44}/(C_{11}+C_{33}-2C_{13})$	0.7	0.3	0.4	0.4	0.4	0.4
$A_3=C_{44}/C_{66}$	0.9	0.8	0.9	1.0	0.9	0.9
Shear (G)		67	72	74	70	70
Bulk (B)		199	197	195	184	181
B/G		2.97	2.74	2.64	2.63	2.59
Young (E)		180	192	198	187	186

The thermal coefficient of linear expansion (α) with temperature is evaluated in Figure 4. The Ru is observed to have decreased bond length corresponding to lower value of α followed by Co, which indicate that the ternaries have higher melting points. On the contrary the higher values of α indicates that the structures expanded more, which was observed for both Zr and Hf, respectively. It can also been seen from the plot that the higher the value of α, implies reduced the transformation temperature.

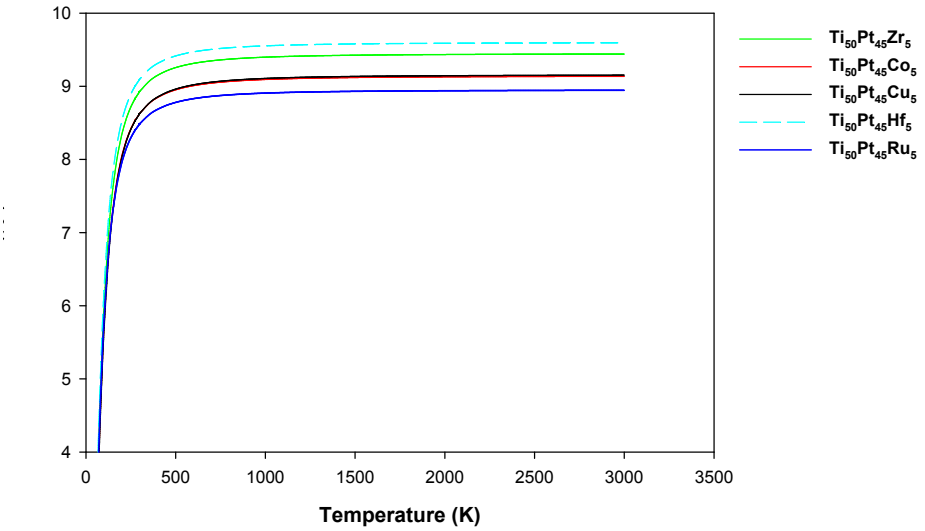

Figure 3. The graph of thermal coefficient of linear expansion against temperature for $Ti_{50}Pt_{45}M_5$ (M=Ru, Co, Cu, Zr and Hf) alloys.

4. Conclusion

First principle approach was used to study the mechanical stability of the B19 $Ti_{50}Pt_{45}M_5$ (M= Ru, Co, Cu, Zr and Hf) atomic composition. The mechanical properties of the ternary structures were investigated using the supercell approach. The thermodynamic stability for the ternary system was investigated by partially substituting some of the Pt with M, M= Ru, Co, Cu, Zr and Hf. It was observed that $Ti_{50}Pt_{45}Ru_5$ is the most stable structure, with the expansion of $Ti_{50}Pt_{45}Zr_5$ and $Ti_{50}Pt_{45}Hf_5$ being the least stable structures. We found the correlation with regard to mechanical stability of the ternaries (C' being positive), the competition between $Ti_{50}Pt_{45}Ru_5$ and $Ti_{50}Pt_{45}Co_5$ gave rise to Co substitution being the most mechanically stable ternary structure. It was also observed from the thermal coefficient of linear expansion that $Ti_{50}Pt_{45}Zr_5$ and $Ti_{50}Pt_{45}Hf_5$ reduced transformation temperature more than $Ti_{50}Pt_{45}Ru_5$ and $Ti_{50}Pt_{45}Co_5$.

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