Computational modelling study of the $Ti_{50}Pt_{50-x}Cu_x$ shape memory alloys

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Abstract. Recently, there is a high demand of shape memory alloys that can be used at high temperatures. TiPt is found to be one of the promising alloys with the martensitic transformation temperature of 1300 K. Previous studies showed that the alloy is mechanically unstable with the negative C′ modulus at 0 K. In order to enhance the mechanical properties of the alloy, a third element Cu was substituted in the TiPt. The stability of the structures with respect to their equilibrium lattice parameters and heats of formation were determined using the density functional theory method embedded in VASP code. It was found that increasing Cu content stabilizes the TiPt with a positive C′ observed for 18.25 at.% Cu. Furthermore, we investigated the temperature dependence of the lattice parameters and copper is found to be lowering the martensitic transformation temperature of the TiPt shape memory alloy.

1. Introduction

Shape memory alloys (SMAs), are metallic systems that remembers their original shape when exposed to a certain pressure or temperature. The shape memory effect and pseudo-elasticity of these materials which accounts for the specific way the phase transformation occurs, makes them remarkably different from other materials. Although they have been used commercially, new applications continue to be developed for SMAs [1]. Some of the applications include actuators and medical stents [2, 3, 4, 5]. There is a growing need SMAs that can be used at high temperatures and only a limited number of such alloys have the potential to be high temperature shape memory alloys (HTSMAs). There has been studies reported on the Ti (Ni,Pt) [6, 7, 8] and Ti (Ni,Pd) [9, 10, 11] where the third element addition effect was investigated . However the martensitic transformation temperature (T_m) of these alloys remained below 830 K. The T_m of TiPt is much higher, at approximately 1273 K [12] and this is considered to be of potential technological interest for elevated temperature SMAs applications. It also undergoes a B2-B19 martensitic phase transformation with a transition temperature above 1300 K [12]. However it has been reported that Ti-Pt based alloys exhibit very low shape memory effect due to low critical stress for slip deformation compared to the stress required for martensitic transformation [13, 14] hence it is necessary to enhance the mechanical properties of the equi-atomic alloy for it to be used at higher temperatures. Previous studies suggested that additions of Co, Ni, and Pd on the TiPt lowered the Tm of the TiPt at 6.25 at.% whereas Ir addition increased the martensitic transformation temperature [15, 16]. In this work we investigate the effect of partial substitution of Pt with Cu on the cubic TiPt potential shape memory alloy system using the supercell approach. The equilibrium lattice parameters and elastic constants are studied using density functional theory (DFT) in this paper for the $Ti_{50}Pt_{50-x}Cu_x$ (x=6.25, 18.75 and 25).

In addition; the temperature effect on the B19 orthorhombic phase is investigated using LAMMPS code [15] which is embedded in Materials Design and the results are compared with the available experimental findings.

2. Methodology

The study employed the density functional theory (DFT) method as implemented in the Vienna *ab initio* simulation package VASP [16, 17, 18, 19] with the projector augmented wave (PAW) [20]. An energy cutoff of 500 eV was used as it was sufficient to converge the total energy of the TiPt alloys. For the exchange-correlation functional, the generalized gradient approximation of Perdew and Wang (GGA-PBE) [15] was chosen. The Brillouin zone integrations were performed for suitably large sets of k-points according to Monkhorst and Pack [21]. A 2x2x2 supercell of TiPt with 16 atoms was used to substitute some of the Pt with Cu. Semi-empirical embedded atom method (EAM) interatomic potentials of Zhou_2004 [22] incorporated in LAMMPS code [23] were employed to study the temperature effect on the lattice parameters of B19 orthorhombic phase. A 5x5x5 supercell of B19 $Ti_{50}Pt_{50-x}Cu_x$ (x=6.25, 18.75 and 25) having 1024 atoms was used. The minimum and maximum temperatures were set to 100 and 1800 K; respectively. The NPT ensemble integration for 100 ps with timestep of 2 fs was used.

3. Results and discussion

3.1 Elastic properties

In Table1 we show the calculated lattice parameters and elastic properties of the $Ti_{50}Pt_{50-x}Cu_x$ (x=6.25, 18.75, 25). The lattice parameters of the TiPt cubic phase decrease minimally with the addition of Cu content as can be observed in Table 1. Previously, the work on the pure structures of TiPt showed that B2 structure was unstable with the C′ of -32 GPa at 0 K. In this work, when 6.25 at.% of Cu is added, the C_{11} becomes less than C_{12} resulting in a negative C′ which is unstable according to the criterion of the elastic constants [24]. Interestingly, the 18.75 at.% Cu addition increases the C′ of TiPt which suggest that at this concentration, the transformation temperature is reduced. It is argued that higher anisotropy A is a sufficient condition for B2-B19 martensitic transformation. However, smaller A indicates that there is a stronger correlation between C_{44} and C′. The origin of B19′ phase is a result of the coupling between C_{44} and C′ just as proposed by Ren and Otsuka [25].

Table 1. Elastic properties (GPa) of $Ti_{50}Pt_{50-x}Cu_x$ ternaries and their anisotropy A using the supercell approach.

Structures	Lattice parameters	C_{11}	C_{12}	C_{44}	C'	A
TiPt [3]	3.18	145	210	45	-32	
$Ti_{50}Pt_{43.75}Cu_{6.25}$	3.16	180	190	54	-10	
$Ti_{50}Pt_{31.25}Cu_{18.75}$	3.13	181	166	49	7.5	7
$Ti_{50}Pt_{25}Cu_{25}$	3.11	179	158	57	10.5	5

The C_{44} can be understood that is 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′ transformation [28]. The calculated elastic constants at 25 at.% Cu are all positive indicating the mechanical stability of the structure. The anisotropy A of both 18.75 and 25 at.% of Cu is larger but positive suggesting the B2 to B19 martensitic transformation.
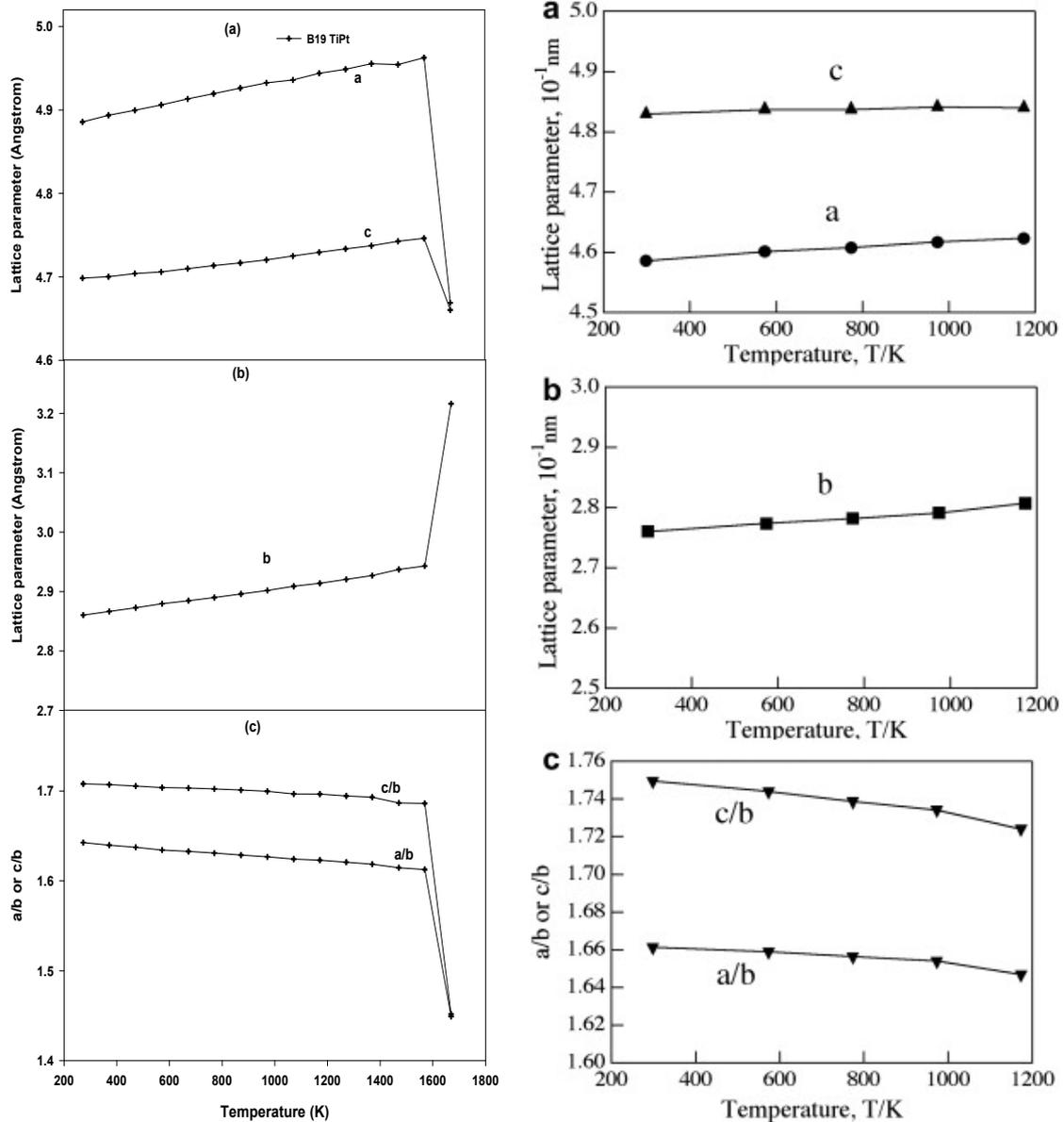
Figure 1: The effect of temperature on the a, c, b, c/b and a/b lattice parameters of the B19 TiPt on the left hand side compared with the experimental results [14] on the right hand side

3.2 Lattice expansion

In Figure 1, the lattice expansion of the B19 orthorhombic phase with temperature for this work is compared with the experimental findings. The lattice parameters of *a* and *c* increase linearly with an increase in temperature. Interestingly, the lattice parameters collapses at approximately 1570 K for both *a* and *c*. The *b* lattice parameter increases linearly with an increase in temperature where a drastic increase is observed at approximately 1570. Yamabe-Mitarai *et al.* investigated the temperature dependence of the lattice parameters for the B19 TiPt experimentally [14] and their results trends are comparable with our findings as shown in Figure 1. The plots of *c/a* and *a/b* ratios are also shown in Figure 1 and decrease linearly with an increase in temperature. Lattice correspondence between the B2 and B19 phase are $[101]_{B2}//a[100]_{B19}$, $[-101]_{B2}//c[001]_{B19}$ and $b[010]_{B2}//b[010]_{B19}$.

The ratios *a/b* and *c/b* should be closer to 1.414, with an increase in temperature, for the B19 to cubic B2 transformation to occur. In Figure 1 (c), *a/b* and *c/b* ratio of the B19 TiPt is 1.451 at approximately 1670 K for this study. The percentage error of the estimated ratio is within 3 % which may suggest that at approximately 1670 K the B19 phase has transformed into cubic B2 phase.
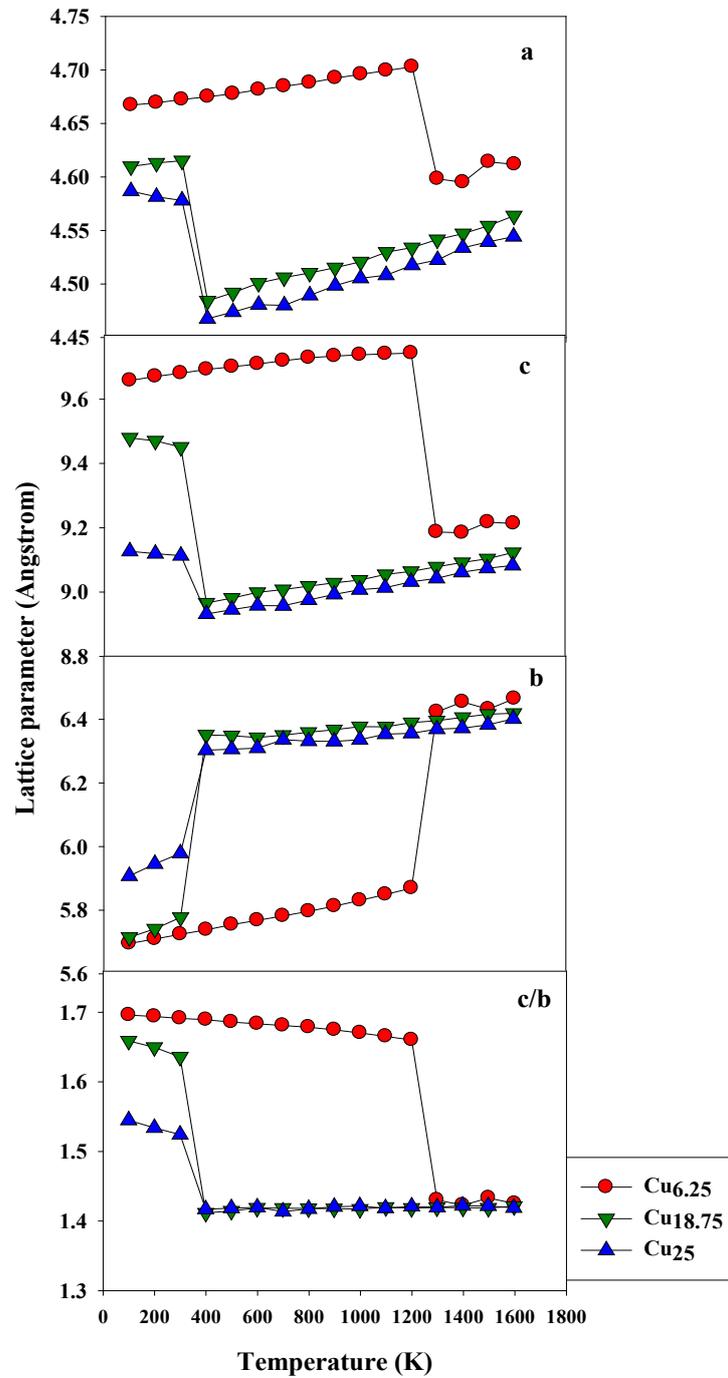
Figure 2. The effect of temperature on the a, c, b and c/b lattice parameters of the B19 TiPt and $Ti_{50}Pt_{50-x}Cu_x$ (x= 6.25, 18.75 and 25)

In Figure 2, we show the plots of lattice constants of $Ti_{50}Pt_{50-x}Cu_x$ with temperature. It is observed that when 6.25 at. % content of Cu is added to the system, the lattice parameter expands linearly and collapses at temperatures of approximately 1200 K which is lower than that observed in Figure 1 for a pure B19 TiPt structure. The c/b ratio is found to be 1.43 at this concentration which can imply that at this point, a transformation to B2 cubic phase is reached. Addition of more content of Cu in the TiPt reduces the transformation temperature drastically as can be observed on the plots of both 18.25 and 25 at.% of Cu. Their lattice parameters collapses at temperatures of about 300 K respectively whereas the 1.41 ratio of c/b is observed at 400 K this suggests that more content of Cu in the TiPt system decreases the transformation temperature of the system.

4. Summary and conclusion

Computational modelling study on the elastic properties and temperature variation in the $Ti_{50}Pt_{50-x}Cu_x$ were performed. The addition of Cu content in TiPt cubic phase was found to be increasing the C′ moduli of the phase leading to a positive anisotropy. The elastic constant of both 18.25 and 25 at.% of Cu were found to be stable with all the moduli obeying the elastic stability criterion. Temperature dependence of the lattice parameters were also studied wherein the pure B19 results are comparable with the experimental findings. Smaller amount of Cu addition lowers B19 to B2 phase at temperatures of approximately 1200 K whereas 18.25 and 25 at.% of Cu content reduces the transformation temperature drastically.

Acknowledgements

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