The elastic properties and the phonon dispersions of TiPtCo shape memory alloy using the supercell approach

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Abstract. Shape memory alloys (SMAs) are classified as a group of metallic materials that has the ability to retain or remember their original shape or size when subjected to the appropriate thermal deformation processes. In general, these materials can easily be elastically or plastically deformed at some relatively low temperature, and upon exposure to some higher temperature can return to their original shape. The effect of substituting Pt with Co as the third element in the TiPt shape memory alloy system using the supercell approach has been investigated. The elastic properties of the TiPtCo high temperature were investigated by using the *ab initio* approach employed in VASP.

1. Introduction

Shape memory alloys (SMAs) are classified as group of metallic materials that has the ability to retain or remember their original shape or size when subjected to the appropriate thermal deformation processes. In general, these materials can easily be elastically or plastically deformed at some relatively low temperature, and upon exposure to some higher temperature can return to their original shape.

Some of the known SMAs include nickel titanium (NiTi), nickel titanium copper (NiTiCu), copper aluminium nickel (CuAlNi) and many other metallic alloy systems [1]. Although they have been around for over half a century, new applications continue to be developed for SMAs [2]. Titanium based SMAs have been widely used in the fields of engineering and medicine due to their shape memory effect and super-plasticity which are displayed in martensitic transformations [3]. Some of the applications include actuators and medical stents [3, 4, 5, 6].

Relatively a wide range of alloys are known to exhibit the shape memory effect (SME), however only those that can recover substantial amounts of strain or that generate significant force upon changing shape are of commercial importance [2]. Many aspects of the transformation are still not well understood [7, 8] even though many theoretical and experimental studies have been devoted to these extraordinary phenomena. There is a growing need of 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). Some of them include Ti(Ni,Pt) [9, 10, 11] and Ti(Ni,Pd) [12, 13, 14, 15, 16, 17]. However, the T_m of TiPt is much higher, at approximately 1000°C [18] and this is considered to be of potential technological interest for elevated temperature SMA applications. It also undergoes a B2-B19 martensite phase transformation with a transition temperature of approximately 1050°C [18] and this can be observed on the Ti-Pt phase diagran shown in figure 1 [19]. In this work we look at the effect of substituting some of the Pt with Co in the B2 TiPt alloy *i.e.* $Ti_{50}Pt_{50-x}$ Co_x using the supercell of 16 atoms of TiPt.

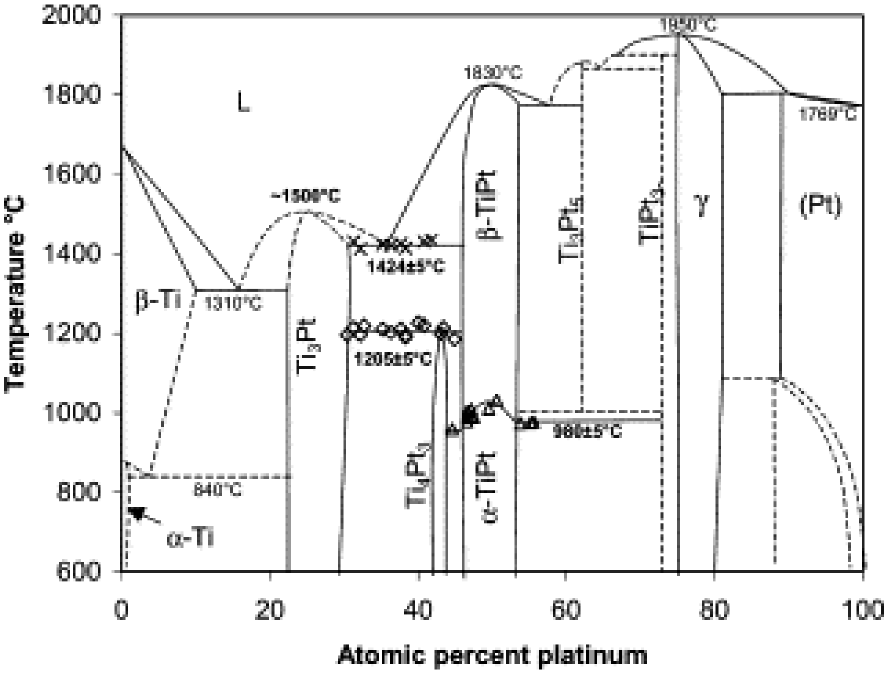


Figure 1. The phase diagram of of the Ti-Pt alloys. The area of interest is at the 50 at. % Pt where the low temperature α-TiPt also known as B19 and the high temperature phase β-TiPt known as B2 exists [19].

2. Methodology

The calculations were carried out using *ab initio* density functional theory (DFT) formalism as implemented in the VASP total energy package VASP [20] with the projector augmented wave (PAW) [21]. 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) [22] was chosen. The Brillouin zone integrations were performed for suitably large sets of *k*-points according to Monkhorst and Pack [23]. A 2x2x2 supercell of TiPt with 16 atoms was used to substitute some of the Pt with Co. The phonon dispersion spectra were evaluated using PHONON code [24] as implemented in Materials Design within MedeA software of VASP code. A *k*-point mesh of 3x3x3 was used. The phonon dispersions and phonon densities of states for the structures were calculated in the framework of the direct method, for which the force constants were derived by a supercell approach.

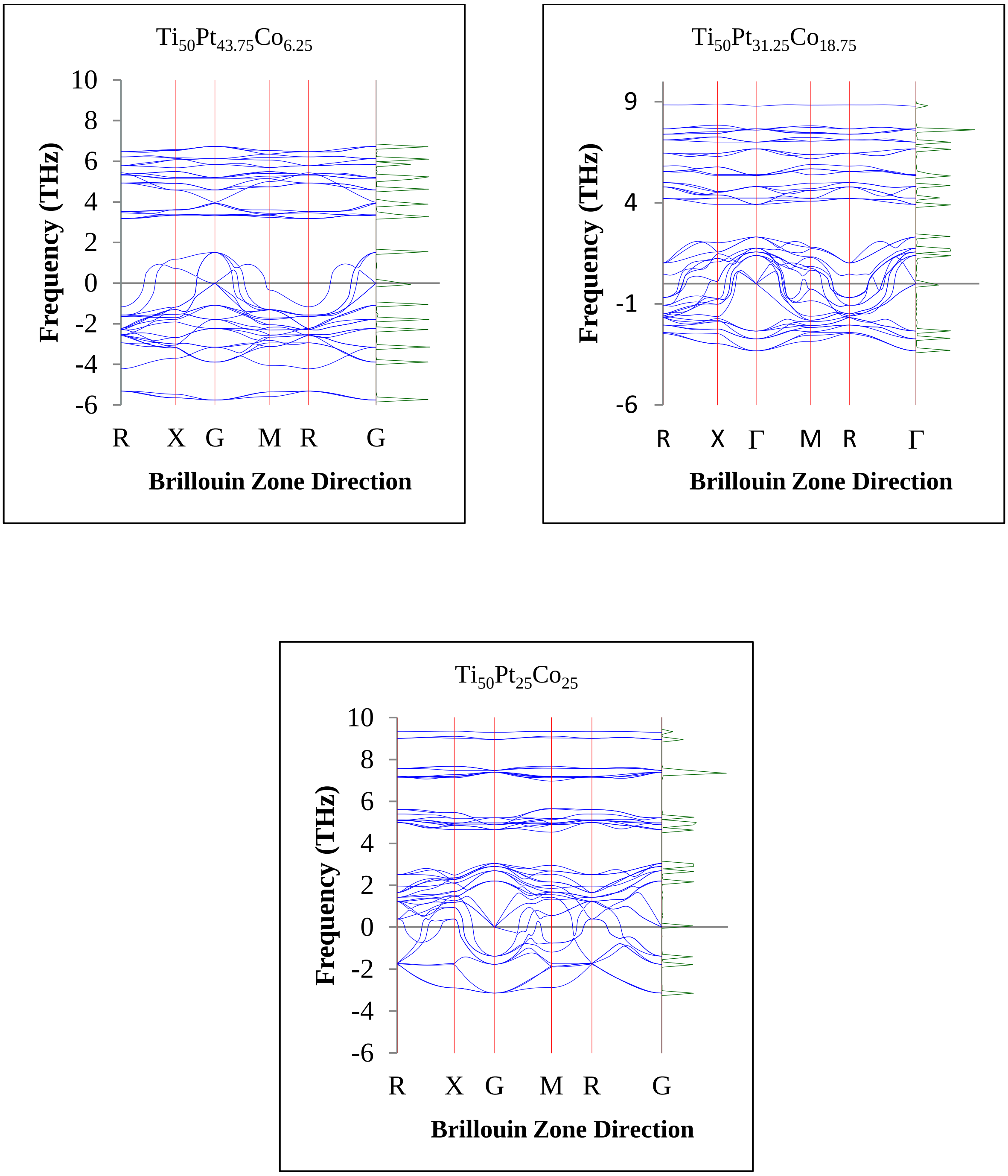
3. Results and discussion

In table 1, we show the calculated lattice parameters and elastic properties of the $Ti_{50}Pt_{50-x}Co_x$ (x=6.25, 18.75, 25). The calculated results show that as we increase the Co concentration in the system the lattice parameter decreases. The calculated elastic constants are all positive indicating the mechanical stability of the structures. 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]. 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 [26]. The C′ at x=6.25 is rather smaller as compared to the other concentrations which results in a larger *A*, this indicates that at this concentration B2 to B19 martensitic transformation occurs. The *A* at x=18.75 and 25 becomes smaller as we increase the Co content indicating a good correlation between the C_{44} and C′. At this (x=18.75 and 25) concentrations there is a B2 to B19' transformation. The C' shear of the B2 TiPt was found to be negative in the previous study and the addition of Co indicates that the C' of the calculated concentrations is positive. It can be inferred from this findings that the addition of Co reduces the martensitic transformation temperature of the cubic TiPt phase since our study suggest more stable phases of $Ti_{50}Pt_{50-x}Co_x$.

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

Structures	Lattice parameters	C_{11}	C_{12}	C_{44}	C'	*A*
[27]TiPt	3.19	145	210	45	-32	
$Ti_{50}Co_{6.25}Pt_{43.75}$	3.15	200	184	35	8	4.37
$Ti_{50}Co_{18.75}Pt_{31.25}$	3.11	212	172	51	20	2.55
$Ti_{50}Co_{25}Pt_{25}$	3.07	260	155	55	52	1.05

The analyses of the vibrational properties of the structures with respect to the phonon dispersion and phonon densities of states were also calculated and are shown in figure 2. There are soft modes observed on the curves suggesting the instability of the phases with respect to the vibrations of the atoms. This is not surprising since it is well known that B2 TiPt is a high temperature phase and it is highly unstable at 0K. The results indicate that substituting Pt with Co reduces the negative frequencies of the TiPt. At x=6.25 the frequency is found to be -6.00THz at the gamma point and as we increase the concentration to x=18.5 the frequency is found to be -3.31 THz. The phonons of $Ti_{50}Pt_{50-x}Co_x$ at x=25 also reduced to the frequency of -3.11THz which is more stable than the other concentrations.



$Ti_{50}Pt_{43.75}Co_{6.25}$

$Ti_{50}Pt_{31.25}Co_{18.75}$

$Ti_{50}Pt_{25}Co_{25}$

Figure 2. Phonon dispersion curves of the different concentration of TiPtCo.

4. Summary and conclusion

The supercell approach method was used to investigate the addition of the third element in the TiPt alloy. As the Co concentration is increased in the system, the lattice parameter decreases. The calculated elastic properties were found to be mechanically stable as opposed to the binary TiPt which has a negative C′. It is evident from our results that the addition of Co reduces the martensitic transformation temperature and this is due to the higher values of C′. The phonon dispersion curves were also calculated and suggest that the addition of Co stabilises the TiPt since it reduces its vibrational soft modes.

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