Ab Initio Study of Martensitic Transformation in NiTiPt High Temperature Shape Memory Alloys

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Abstract: The crystal structures and martensitic transformation of Ti50Ni50−xPt x alloys (x = 0, 6.25, 8.33, 10.42, 12.5, 18.75, 25) were studied by means of density functional theory (DFT). The computational results indicate that the lattice parameters of Ti-Ni-Pt alloys continuously increase with increasing the Pt content. It is found that at ≤ 12.5 at.% Pt, the martensite structure is monoclinic B19′ phase, and the energy differences between parent and martensite phases (∆E) decrease slightly with a minimum observed at 6.25 at.% Pt. However, when the Pt content is increased to around 15 at.%, the most stable martensite phase is the orthorhombic B19 structure, and the ∆E increases sharply with Pt concentration. It was found that the phase transition temperatures are closely related to the energy differences ∆E between parent and martensite phases. The electronic structures of martensite B19 and B19′ phases are also discussed.

Keywords: NiTiPt; high temperature shape memory alloys; martensitic phase transformation; density functional theory; electronic structure

1. Introduction

NiTi shape memory alloys (SMAs) exhibit the shape memory effect and superelasticity which are attributed to reversible thermoelastic martensitic transformations (MTs). The NiTi alloys have found diverse commercial use in biomedicine and engineering applications since 1963 [1,2]. The structure, mechanics, and martensitic phase transformation in binary NiTi shape memory alloy were widely studied [3–7]. As is known, the dependence of the phase transformation temperature on alloy composition is of utmost importance with regard to the application of NiTi SMAs [2,8]. Some alloying additions, for example, Fe, Co, Al, Mn, V, or Cr will decrease the martensite start temperatures (Ms) of NiTi-based alloys [8, 9]. Unfortunately, some special applications such as aerospace, automotive and power generation, and chemical processing industries demand a high transition temperature, which are greatly limited due to the low Ms.

Over the past decades, considerable efforts have been made in developing high-temperature shape memory alloys (HTSMAs) with significantly elevated transformation temperatures based on ternary NiTiX (X = Pd, Pt, Au, Hf, and Zr) compositions [10]. Experimental studies indicate additions of hafnium above 3 at.% increase the transformation temperatures of Ti-Ni-Hf alloys [11]. For NiTi alloys, replacing titanium or nickel with Zr or Pd above 10 at.% can increase the transformation temperatures [12,13]. There are many reports on the crystal structures [11,14–17], phase transformations [18–24], shape-memory behaviors [12,25–29], and precipitate phases [30–34] in NiTiX (X = Pd, Hf, and Zr) alloys.

Of these HTSMAs, the (Ni,Pt)Ti system, owing to the highest potential use temperature, in spite of the high costs, has been studied as the promising SMAs for demanding applications, such as in the aerospace, automotive, power generation, and chemical processing industries. Yet, compared to the NiTiX (X = Pd, Hf and Zr) alloys, Ti-Ni-Pt alloys have not received a similar level of attention. Recently, Rios et al. [35] reported that the
The martensitic transformation temperature of the TiNiPt system increases sharply when Pt content exceeds 10 at.%. The \( M_s \) can be increased to near 1000 °C in TiPt alloy. Moreover, NiTiPt alloys show the low thermal hysteresis [36,37], good work output [38], and excellent oxidation resistance [39].

The elastic property of the B2 phase in NiTiPt has been investigated by density functional theory (DFT) [40,41]. To the best of our knowledge, few studies discuss the mechanism of phase transition. No theoretical study on the martensitic transformations of TiNiPt has been published. DFT has been used successfully to examine the influence of the Hf, Pd, Cu, or Zr on NiTi properties [42–47]. Consequently, the MTs of ternary TiNiPt HTSMAs as a function of the Pt content is investigated in the present research by first principles.

2. Model and Methodology

NiTi B2, orthorhombic B19, and monoclinic B19\(^{\prime}\) structures taken from our previous work [47] are adopted in the present study. Note that we employ the parent NiTi body-centered tetragonal (bct) lattice. The structural parameters of bct are \( a = a_0, \ b = c = \sqrt{2}a_0 \), here \( a_0 \) is the lattice constants of cubic B2 NiTi structure. In addition, we focus on the B19 and B19\(^{\prime}\) structures for the martensite phase reported in the literature [3,5,48]. The structures and parameters of B19 and B19\(^{\prime}\) are very close to each other, except the monoclinic distortion from 90° to \( \beta = 98.26^\circ \). Considering the symmetry of the cell, \( 3 \times 2 \times 2 \) supercells of the B2, B19, and B19\(^{\prime}\) are constructed containing 48 atoms for the present simulation.

The different site occupations of Ni atoms in the austenite B2 \( 3 \times 2 \times 2 \) supercell Ni\(_{24}\)Ti\(_{24}\) structure, shown in Figure 1, are indicated by smaller blue spheres and labeled with numbers. A survey of the literature [9] reveals that the addition of Pt prefers to occupy the Ni rather than Ti sites in TiNiPt alloys. In this study, replacing nickel with platinum, we adopt the Ti\(_{39}\)Ni\(_{50-\delta}\)Pt\(_{\delta}\) alloys (\( x = 0, 6.25, 8.33, 10.42, 12.5, 18.75, 25 \)) alloys as our models. Geometry optimizations were implemented for all possible doping structures. The most stable structures were calculated with the principle of the lowest energy. Table 1 presents the site occupation of Pt in the parent phase of Ti-rich Ni-Ti-Pt alloys.

![Figure 1](image-url). Ni occupancy in the austenite B2 \( 3 \times 2 \times 2 \) supercell Ni\(_{24}\)Ti\(_{24}\) structure. Smaller blue spheres denote Ni atoms; larger gray spheres denote Ti atoms. The \( 3 \times 2 \times 2 \) supercells of B19 and B19\(^{\prime}\) are also used, and structures are similar to that of B2.
Table 1. The site preference of Pt additions in the austenite B2 \(3 \times 2 \times 2\) supercell structure at different doping concentrations, \(n\) is the number of Pt atoms in the supercell.

| \(n\) | Pt content (at.\%) | Site Occupation of Pt |
|-------|--------------------|----------------------|
| 3     | 6.25               | 8, 11, 24            |
| 4     | 8.33               | 8, 11, 24, 18        |
| 5     | 10.42              | 5, 8, 11, 24, 18     |
| 6     | 12.50              | 2, 5, 8, 11, 24, 18  |
| 9     | 18.75              | 3, 5, 8, 9, 11, 16, 17, 22, 24 |
| 12    | 25.00              | 3, 5, 6, 8, 10, 11, 14, 16, 17, 19, 22, 24 |

The present calculations are performed within the framework of DFT as implemented in the Vienna ab initio simulation package [49–51] (VASP) code, applying the generalized gradient approximation [52] (GGA) and a projected augmented wave [53] (PAW) basis. We chose a 500 eV plane-wave energy cutoff and the \(4 \times 4 \times 4\) \(k\)-points [54] for the \(3 \times 2 \times 2\) supercells of the B2, B19, and B19’ phases in TiNiPt alloys.

In order to analyze the phase stabilities of B2, B19, and B19’ of Ni-Ti-Pt alloys with the increasing of the Pt content, we evaluate the energies of formation, \(E_f\) [55–57]. Formation energies per atom of Ti\(_{50}\)Ni\(_{50-x}\)Pt\(_x\) alloys are calculated as:

\[
E_f = \frac{E_{\text{tot}}(\text{Ti}_{50}\text{Ni}_{50-x}\text{Pt}_x) - 50E_{\text{Ti}} - (50 - x)E_{\text{Ni}} -xE_{\text{Pt}}}{100}
\]

where \(E_{\text{tot}}(\text{Ti}_{50}\text{Ni}_{50-x}\text{Pt}_x)\) is the total energy of TiNiPt alloys. \(E_{\text{Ni}}\), \(E_{\text{Ti}}\), and \(E_{\text{Pt}}\) denote the energies per atom of the pure Ni, Ti, and Pt in their bulk states, respectively.

The transformation behaviors as a function of the doping concentration can be described by the total energy differences \(\Delta E_{\text{A-M}}\) between the austenite and martensite phases. According to the laws of thermodynamics, the Gibbs free energy \(G\) are defined as:

\[
G = U - TS + PV
\]

where \(U\), \(T\), \(S\), \(P\), and \(V\) are the internal energy, temperature, entropy, pressure, and volume, respectively. From the point of the thermodynamics of phase transition, at the equilibrium temperature \(T_m\), the free energies of the austenitic and martensitic phases are equal, i.e.,

\[
\Delta C^{\text{A-M}} = \Delta U^{\text{A-M}} - T_m\Delta S^{\text{A-M}} + P\Delta V^{\text{A-M}} = 0.
\]

For solid state phase transition,

\[
P\Delta V^{\text{A-M}} \approx 0.
\]

Thus,

\[
\Delta U^{\text{A-M}} = T_m\Delta S^{\text{A-M}}.
\]

Generally, the DFT calculations are implemented at the temperature of 0 K. The \(\Delta U^{\text{A-M}}\) is approximately equal to the total energy differences \(\Delta E^{\text{A-M}}\). So,

\[
\Delta E^{\text{A-M}} = T_m\Delta S^{\text{A-M}}
\]

\[
\Delta E^{\text{A-M}} \propto T_m
\]

\(T_m\) usually increases with the increasing of \(\Delta E^{\text{A-M}}\). Therefore, the \(\Delta E^{\text{A-M}}\) between B2 and B19 (or B19’) structures can be used to discuss the phase transition temperature \(T_m\). A larger energy differences \(\Delta E^{\text{A-M}}\) indicate the higher martensite start temperature \(M_s\), as has been shown in the literature [47,55,58–60].

A schematic diagram of our study is presented in Figure 2. We first construct the computational models, then solve the Kohn–Sham equations, obtain the lattice parameters,
and the total energies as a function of the doping concentration. We evaluate the phase stabilities of TiNiPt alloys via calculating the formation energies $E_f$. At last, we describe the martensitic transformation through the energy differences between austenite and martensite phases in TiNiPt alloys.

Figure 2. Research schematic diagram.

3. Results and Discussion
3.1. Crystal Structures of TiNiPt Alloys

At first, the calculated lattice parameters of B2, B19, and B19′ phases of NiTi presented in Figure 3, which are in good agreement with the experimental and theoretical data [48,61–64]. Generally the lattice volume depends on both the size of the constituent atoms and the number of valence electrons of the intermetallic crystal [65]. In ternary TiNiPt alloys, the valence electrons per atom are calculated as [11,42,66]:

$$\frac{e_v}{a} = f_{Ni}e_{Ni}^{v} + f_{Ti}e_{Ti}^{v} + f_{Pt}e_{Pt}^{v}$$

where $f_{Ni}, f_{Ti},$ and $f_{Pt}$ represent the atomic fractions of elements, and $e_{Ni}^{v}, e_{Ti}^{v},$ and $e_{Pt}^{v}$ are the corresponding number of valence electrons, i.e., $e_{Ni}^{v} = 4, e_{Ti}^{v} = 10,$ and $e_{Pt}^{v} = 10$, according to the valence electron configurations: Ti-3$d^2$4$s^2$, Ni-3$d^8$4$s^2$, and Pt-5$d^9$6$s^1$.

Substituting Ni with Pt, the number of valence electrons per atom of Ti$_{50}$Ni$_{50-x}$Pt$_x$ alloys remains a constant 7. Thus, the supercell volume mainly depends on the size of the constituent atoms. The atomic radii of Ni, Ti, and Pt are 1.25 Å, 1.45 Å, and 1.36 Å, respectively. The lattice parameters $a, b, c$ and the lattice volumes of the NiTiPt alloys expand consistently with increasing Pt content in B2, B19, and B19′ structures (see Figure 3). This can be attributed to the larger atomic size of Pt than of Ni atoms.
3.2. Phase Stabilities of Ti$_{50}$Ni$_{50-x}$Pt$_x$ Alloys

Before rationalizing the strong dependence of the martensite start temperature on alloy composition in ternary Ni-Ti-Pt shape memory alloys from first-principles calculations, we examine the transformation pathways of Ti$_{50}$Ni$_{50-x}$Pt$_x$ alloys ($x = 0, 6.25, 8.33, 10.42, 12.5, 18.75, 25$).

In Figure 4, we plot the calculated $E_f$ as a function of the Pt concentration. The binary NiTi alloy can be considered as a TiNiPt alloy containing zero at.% Pt. Above all, as can be seen from Figure 4, in equiatomic NiTi binary alloys, the B2 phase, which is only stable at high temperatures, exhibits the highest value of $E_f$; the B19$'$ martensitic structure with the lowest formation energy is the most stable one. They are in excellent agreement with the previous experimental observations [67] and computational results [48].

Furthermore, the overall trend as presented in Figure 4 shows that the $E_f$ of B2, B19, and B19$'$ decline almost linearly with the increasing of Pt doping concentration, which indicates that the stability of Ti$_{50}$Ni$_{50-x}$Pt$_x$ alloys becomes better when Ni is replaced by Pt. This can be explained by the electronic hybridization of Pt with Ti and Ni (see Figure 5), and will be discussed in more detail in Section 3.3. We can also note that B2 exhibits the highest formation energy which is one of the most unstable structures among all the structures in the TiNiPt system.

Finally, as shown in Figure 4, when Pt content is between 0 and 12.5 at.%, $E_f$ of monoclinic B19$'$ phases are all negative and lower than that of orthorhombic B19 and B2 phases, thus the most stable phase is the monoclinic martensitic crystal structure. However, as Pt content reaches to near 15 at.%, the orthorhombic phases are more stable compared with the monoclinic phases. It can be seen that the $E_f$ curve of B19 is a little steeper than that of B19$'$, thus a crossover exists for Pt content about 15 at.%, which can be attributed to the different bond lengths of Ni-Ti in B19 and B19$'$. The shortest Ni-Ti bond length of B19$'$ (2.514 Å) is smaller than that of B19 (2.564 Å), which leads to slightly more repulsive interaction in B19$'$ compared to that of B19 with the doping of Pt atoms.
Figure 4. The formation energies, $E_f$, of the austenite B2, martensite B19 and B19' phases as a function of Pt content in ternary Ti$_{50}$Ni$_{50-x}$Pt$_x$ alloys.

Figure 5. Partial density of states (PDOSs) of martensite (a) B19' and (b) B19 phase of Ti$_{50}$Ni$_{50-x}$Pt$_x$ ($x = 0, 12.5, 18.75$) alloys for the Ti, Ni, and Pt site. The vertical line denotes the Fermi level, which is located at 0 eV.
Therefore, it can be expected that the transformation path would be B2 to B19' at Pt content less than about 15 at.%, while B2 to B19 at Pt content greater than 15 at.%. As the experimental observations [10] show that, at ≤ 10 at.% Pt, the martensite structure is monoclinic B19', at higher levels of Pt, at least 16 at.% or greater, the martensite orthorhombic B19 is formed. This means that our calculated result is consistent with the experimental result.

3.3. Electronic Structures

In order to investigate the electronic mechanism behind the martensitic transformation pathways, the partial density of states (PDOSs) of the B19 and B19' structures of Ti50Ni50−xPtx alloys are calculated and plotted in Figure 5. For NiTi, the electronic states below the Fermi level are mostly contributed by the Ni d states, while electronic states above the Fermi level come mainly from Ti d states. This feature is consistent with other DFT study [46]. Furthermore, the hybridization between Ti d and Ni d states in the structure of B19' is stronger than that of B19. Moreover, compared with the Ti d of B19 NiTi, the high energies above Fermi level of B19' shift towards the Fermi level. This suggests that B19' is more stable than B19 in NiTi, in accordance with the results of $E_f$.

Figure 5 shows that, due to the Pt dopants, a new set of peaks centered at −4.5 eV emerges in the PDOSs of the B19 and B19' of Ti50Ni50−xPt5 serials. Moreover, these set of peaks become stronger and broader with the increase of Pt content. The doping of Pt gives rise to the strong resonant states between the Ni and its nearest neighbor Pt atoms in the energy region from −3 eV to −1.8 eV, and enhances the interaction between Ti and Ni (Pt) atoms. The peaks of Ti atoms and Ni-Pt resonated atoms shift towards lower energies slightly. These indicate that both the B19 and B19' phases become more stable as the Pt increases, in line with the data of $E_f$. The electronic interaction in B19' is slightly stronger than that of in B19.

However, for the $x = 18.75$ alloy, the peaks of Ni d states below the Fermi level located at about −1.8 eV in the PDOSs of B19 are higher than those of B19', which implies that the hybridization between Ni (Pt) d and Ti d states in the B19 phase is stronger than that of B19'. This reveals that the B19 orthorhombic phase is more stable compared with the B19' monoclinic phase, which is in accordance with the formation energy results that the orthorhombic phase is the martensitic stable structure for Ti50Ni50−xPt5 alloy, as $x > 15$.

3.4. Energy Differences between the Austenite and Martensite

After studying the phase transition path of Ti50Ni50−xPt5 alloys ($x = 0, 6.25, 8.33, 10.42, 12.5, 18.75, 25$), we set out to research the concentration dependence of $M_s$ of these alloys using the density functional theory. At first, we invoke the total energy differences, $\Delta E$, between B2 and martensite (B19 or B19') phases. According to the previous studies [47,55,58–60], there is a strong relationship between $M_s$ and $\Delta E$ from first-principles calculations, i.e., a larger $\Delta E$ corresponds to a higher $M_s$. All these energies are normalized per atom. They are calculated (per atom) as:

$$\Delta E_{B19} = E_{B2} - E_{B19}$$

$$\Delta E_{B19'} = E_{B2} - E_{B19'}$$

with $E_{B2}$, $E_{B19}$, and $E_{B19'}$ being the total energies per atom of B2, B19, and B19' structures of Ti50Ni50−xPt5 alloys, respectively.

At first, the energy differences $\Delta E_{B19} = E_{B2} - E_{B19} = 34$ meV/atom and $\Delta E_{B19'} = E_{B2} - E_{B19'} = 44$ meV/atom for an equiatomic binary NiTi alloy are obtained, which is consistent with other theoretical values [48,61,64,68]. The $\Delta E_{B19}$ and $\Delta E_{B19'}$ are both positive, and the $\Delta E_{B19'}$ is a little higher than $\Delta E_{B19}$ which revealed that the monoclinic B19' is more energetically stable than orthorhombic B19 structures.

Then, the calculated concentration dependence of $\Delta E_{B19}$ and $\Delta E_{B19'}$ for Ti50Ni50−xPt5 alloys ($x = 0, 6.25, 8.33, 10.42, 12.5, 18.75, 25$) are presented in Figure 6. Finally, in order to confirm the experimental observations of alloy composition dependence of $M_s$ in Figure 7,
we plot the total energy differences, $\Delta E$, as well as $M_s$ as a function of the Pt concentration in the Ti$_{50}$Ni$_{50-x}$Pt$_x$ alloys. $M_s$ of Ni-Ti-Pt is cited from Ref. [35].

![Figure 6](image)

**Figure 6.** The energy differences between austenite and martensite ($\Delta E$) as a function of the doping concentration in Ti$_{50}$Ni$_{50-x}$Pt$_x$ alloys.

![Figure 7](image)

**Figure 7.** Compositional dependence of $\Delta E$ and phase transformation start temperature ($M_s$) of Ti$_{50}$Ni$_{50-x}$Pt$_x$ alloys. The data of $M_s$ refer to the right axis and those of $\Delta E$ to the left axis. $M_s$ is cited from Ref. [35].

As presented in Figure 6, the $\Delta E_{B19}$ and $\Delta E_{B19'}$ are both positive. There is a crossover at the $\Delta E$ curve for Pt near 15 at.% concentration, which corresponds to that of $E_f$ in B19 and B19$'$ (see Figure 4), most likely due to the marginal difference in the Ni-Ti bond length previously mentioned. For Pt $<$ 15 at.%, the $\Delta E_{B19'}$ is higher than $\Delta E_{B19}$, which indicates that the monoclinic B19$'$ phase is more stable than orthorhombic B19 structures; whereas for Pt $> 15$ at.%, the $\Delta E_{B19}$ is higher than $\Delta E_{B19'}$, which suggests orthorhombic B19 structures are more stable than the monoclinic B19$'$ phase. These are in line with the present computed results of $E_f$ of Ti$_{50}$Ni$_{50-x}$Pt$_x$ alloys ($x = 0, 6.25, 8.33, 10.42, 12.5, 18.75, 25$) (see Figure 4).
According to the data of $\Delta E$ of the most stable martensite phase, $\Delta E$ and $M_s$ of $\text{Ti}_{50}\text{Ni}_{50-x}\text{Pt}_x$ alloys are presented in Figure 7 as a function of Pt content. First and foremost, it can be found from Figure 7 that the overall trends of the $\Delta E$ and $M_s$ of $\text{Ti}_{50}\text{Ni}_{50-x}\text{Pt}_x$ alloys with the increasing of the Pt concentration are remarkably similar to each other, which confirms that the present calculated results are fully in line with the experimental observations. For Pt $\leq 8.33$ at.%, martensite start temperatures and $\Delta E$ are less sensitive to composition, and decrease slightly with a minimum observed at 6.25 at.% Pt; for 8.33 at.% $< \text{Pt} < 12.5$ at.%, $\Delta E$ and $M_s$ increase slightly. However, at higher levels of Pt, especially exceeding about 15 at.%, $\Delta E$ and $M_s$ increase sharply with Pt content. This can be explained as follows, with the dramatically increasing of $M_s$, correspondingly, more energy is needed for the martensitic transformation. Taking into account good coincidences with the results of experimental studies, the resulting model can be a good tool for simplifying and rationalizing experimental studies of the NiTiPt system.

4. Conclusions

In the present paper we explored the strong dependence of the martensite start temperature $M_s$ on alloy composition in ternary Ni-Ti-Pt shape memory alloys by means of density functional theory. Based on the crystal structure optimizations of $\text{Ti}_{50}\text{Ni}_{50-x}\text{Pt}_x$ ($x = 0, 6.25, 8.33, 10.42, 12.5, 18.75, 25$) shape memory alloys, Pt additions substituted for Ni in NiTi with a supercell approach are calculated. From the results obtained in the present work the following conclusions can be drawn:

- The lattice parameters $a$, $b$, $c$ and supercell volume of $\text{Ti}_{50}\text{Ni}_{50-x}\text{Pt}_x$ alloys increase with the increasing of Pt content. Since the number of valence electrons of Pt is equal to that of Ni, the larger atomic radius of Pt compared to Ni results in a bigger supercell volume.
- As the calculated results of formation energies presented, for Pt $> 15$ at.%, the monoclinic B19′ martensite crystal structure becomes unstable and an orthorhombic B19 crystal structure is formed, resulting from a gradual destabilization/stabilization of B19′/B19, which is in excellent agreement with the experimental data.
- The computational results of the total energy differences $\Delta E$ between parent and martensite phases are as follows: for Pt $< 10$ at.%, the substitution of Pt for Ni has relatively little effect on $\Delta E$ (with a minimum at 6.25 at.% Pt), which shows only a moderate dependence of $\Delta E$ on alloy composition; for Pt $\geq 10$ at.%, the $\Delta E$ increase linearly with increasing Pt content, which brings about the dramatical enhancement of $M_s$.

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