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Effect of Co additions on B2 phase stability of Ni-poor NiTi-based alloys

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ABSTRACT

Based on the generalized atomic site preference model and the quasi-chemical bond approximation, the atomic distribution state free energy of the third addition in a binary alloy with the B2 lattice is derived analytically. The configurational energy coefficients are independent of the alloy composition and can be determined directly by the first principle calculation. The calculated B2 ↔ bcc transformation temperature of the Ni-poor NiTi–Co alloys changes at 200 K at.%$^{-1}$ by the increasing of Co concentration. The experimental results about the effect of the third Co additions on the martensitic transformation procedure of the Ni-poor NiTi-based alloys are well explained.

1. Introduction

In a number of crystalline compounds with around stoichiometric composition and at sufficiently low temperatures, some ordered lattice structures can be formed by the atomic site preference (ASP, each species of atom preferring to occupy only a certain type of site in the crystal lattice). Numerous experimental investigations have indicated that the magnetic, electrical, mechanical and many other properties of the compounds change strongly upon the variation of the ASP state [1]. Consequently, both experimental and theoretical studies of the ASP behaviors are of great practical interest for solving the problem of obtaining solid materials with desired properties and also important for the development of the solid state theory. Particularly, it was pointed out that the shape memory characteristics of NiTi alloys can be related to the site preference behaviors of additions to the base alloy [2]. Experimental research showed that three different phases exhibit in near equiatomic Ni–Ti alloys, the B2 phase, the B19′ phase, and the R-phase [3]. The B2 phase is the high temperature parent phase, the B19′ is the martensite phase (M phase), and the R phase is a rhombohedral phase being incommensurate with the B2 phase [3]. It has been experimentally determined that the B19′ martensite can be obtained either by a single step transformation of B2 ↔ M, or by a two-step transformation of B2 ↔ R ↔ M [3–11]. All the transformations are martensitic in nature [4,12]. The B2 ↔ R transformation can be introduced effectively by additions of third elements [7–9,13,14]. The first principle calculation indicated that the reversibility of the martensitic transformation (MT) in binary NiTi alloys depends strongly on the stabilization of the B2 phase [15]. Knowledge of the relationship between the ASP behaviors of alloying additions and B2 phase stability of NiTi alloys is beneficial to a better understanding of the effects of alloying additions on the martensitic transformation procedure.

Accompanied by the variation of ASP state, various point defects (vacancies and anti-site atoms) will form. The ASP behaviors of alloys are controlled by the formation energies of the point defects. Experimental measurements of the formation energies of point defects may be influenced by many factors and yield drastically different results [16]. In view of the difficulty in the experimental studies, it is highly desirable to determine the formation energy by computation and different calculation methods are developed [2,16–19]. In the present work, the ASP energy of a ternary alloy with B2 structure is derived as a function of the alloy compositions and ASP degrees defined in our previous work [18]. With the theoretical derivation, a simplified first principle calculation method to evaluate the ASP energy in a ternary B2 phase is suggested.

The experimental research shows that the martensitic transformation procedure of NiTi can be a single step transformation of B2 ↔ M, or a two-step transformation of B2 ↔ R ↔ M with different contents of Co additions [8]. As an application of the present ASP energy calculation method, the effect of Co addition on the B2 phase stability of the Ni-poor NiTi-based alloys is evaluated.

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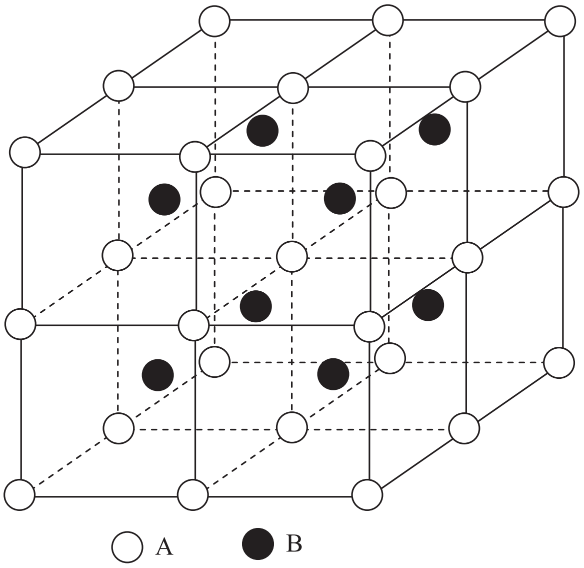

Fig. 1. Initial calculation cell of the first principle calculations.

2. Methodology

In the perfect ordered B2 phase of a stoichiometric AB alloy, the “right” sites for species A and B are defined as sublattice *a* and sublattice *b*, respectively. Without considering vacancy, the atomic distribution state in the B2 phase of ternary $A_{0.5-y-z}B_{0.5+y}X_z$ ($y \geq 0$ and $z \geq 0$) can be described by the ASP degrees of atom α on sublattice *a*, $\eta_{a\alpha}$ (α = A or X), which is defined as [18]

$$\eta_{a\alpha} = \begin{cases} -1 & \text{(atom } \alpha \text{ occupying sublattice } a \text{ with the minimum probability)} \\ 0 & \text{(atom } \alpha \text{ occupying sublattice } a \text{ with the average probability)} \\ 1 & \text{(atom } \alpha \text{ occupying sublattice } a \text{ with the maximum probability)} \end{cases} \quad (1)$$

For convenience, η_{aA} and η_{aX} are abbreviated as η_1 and η_2, respectively in the following. According to the ASP degree definition [18], the set of the atomic site occupation probabilities for the concerned alloy can be expressed in term of η_k (k = 1 and 2) as

$$\begin{pmatrix} P_{aA} & P_{aB} & P_{aX} \\ P_{bA} & P_{bB} & P_{bX} \end{pmatrix} = \begin{pmatrix} C_A(1+\eta_1) & 1-C_A(1+\eta_1)-C_X(1+\eta_2) & C_X(1+\eta_2) \\ C_A(1-\eta_1) & 1-C_A(1-\eta_1)-C_X(1-\eta_2) & C_X(1-\eta_2) \end{pmatrix} \quad (2)$$

where C_α (α = A, B, or X) is the atomic composition of atom α, $P_{i\alpha}$ the probability of atom α occupying sublattice *i* (*i* = *a* or *b*).

In the mean field scheme and the first nearest-neighbor pairwise interaction [18,20], the ASP energy per atom, ΔE, can be derived as

$$\begin{aligned} \Delta E(\eta_1, \eta_2) &= E(\eta_1, \eta_2) - E(0, 0) \\ &= C_A^2 \varepsilon_1 \eta_1^2 + C_X^2 \varepsilon_2 \eta_2^2 + 2C_A C_X \varepsilon_3 \eta_1 \eta_2 \end{aligned} \quad (3)$$

with

$$\varepsilon_1 = 4(2\phi_{AB} - \phi_{AA} - \phi_{BB}) \quad (4)$$

$$\varepsilon_2 = 4(2\phi_{BX} - \phi_{XX} - \phi_{BB}) \quad (5)$$

$$\varepsilon_3 = 4(\phi_{AB} + \phi_{BX} - \phi_{AX} - \phi_{BB}) \quad (6)$$

where $\phi_{\alpha\beta}$ is the first neighbor pair interaction between atom α and β.

As a conventional method, $\phi_{\alpha\beta}$ has to be determined prior to evaluating ε_j (j = 1, 2, and 3). But it is noticed that ε_j is independent of the component concentrations. Take advantage of the composition independence, ε_j can be directly determined by the total energy first principle calculations of a super-cell.

As illustrated in Fig. 1, an initial A_8B_8 supercell composed of 2 × 2 × 2 B2 unite cells is constructed. First the A atom located at the center of the initial super-cell is replaced by a X atom to form A_7B_8X. The ASP state for this case is $\eta_1 = 1$ and $\eta_2 = 1$. With a lattice parameter optimization, the total energy of this configuration is calculated as E_1 and the optimized cell size is a_0. Then the X atom is exchanged with one of the eight B atoms. The ASP state changes to $\eta_1 = 1$ and $\eta_2 = -1$, and the total energy is calculated as E_2 at the cell size a_0. By Eq. (3), ε_3 is determined as

$$\varepsilon_3 = \frac{4}{7}(E_1 - E_2) \quad (7)$$

C_X is zero for the initial A_8B_8 supercell. The second and third terms vanish in this case. The ASP state of the initial supercell is $\eta_1 = 1$ and whose total energy is calculated as E_3 at a_0. Next the A atom located at the cell center is exchanged with one of the eight B atoms and the total energy of the cell is calculated as E_4 at a_0. The ASP state corresponding to E_4 is $\eta_1 = 0.75$. Then by Eq. (3), ε_1 is determined as

Table 1
Optimized lattice constants, supercell total energies and coefficients of ASP energies for Co additions in NiTi-based alloy.

Alloys	NiTi–Co
a_0 (10^{-1} nm)	0.3007
E_1 (eV)	−23,666.300
E_2 (eV)	−23,665.155
E_3 (eV)	−21,176.204
E_4 (eV)	−21,174.032
E_5 (eV)	−23,355.132
E_6 (eV)	−23,353.438
ε_1 (eV/atom)	−0.654
ε_2 (eV/atom)	−0.968
ε_3 (eV/atom)	−1.241

$$\varepsilon_1 = \frac{4}{7}(E_3 - E_4) \quad (8)$$

By substituting eight X atoms for all A atoms in the initial supercell, the system becomes B_8X_8 and C_A is zero. Using the same procedure as that for determining ε_1, the B_8X_8 supercell total energies for $\eta_2 = 1$ and $\eta_2 = 0.75$ are calculated as E_5 and E_6, respectively. Then ε_2 is determined as

$$\varepsilon_2 = \frac{4}{7}(E_5 - E_6) \quad (9)$$

All the supercell total energies are calculated by using Cambridge serial total energy package (CASTEP) enclosed in Material Studio 4.4. The first principle total energy calculations are performed by using the exchange-correlation potential of generalized gradient approximation of Perdew, Burke, and Ernzerhof (GGA-PBE) [21], ultrasoft pseudopotential [22] represented in reciprocal space with PBE exchange-correlation potential, plane-wave basis set cutoff energy of 350 eV, and *k* point mesh of 4 × 4 × 4.

The configuration entropy per atom, *S*, is

$$S = -\frac{k_B}{2} \sum_{i(=\mathrm{Ni,Ti})} \sum_{\alpha(=\mathrm{Ni,Ti,X})} P_{i\alpha} \ln(P_{i\alpha}) \quad (10)$$

where k_B is Boltzmann constant.

Under zero external pressure, the ASP free energy per atom at the absolute temperature *T*, ΔF, is

$$\Delta F(T, \eta_1, \eta_2) = \Delta E(\eta_1, \eta_2) + [S(\eta_1, \eta_2) - S(0)]T \quad (11)$$

Then the temperature-depending atomic site occupation behaviors of the ternary alloy can be estimated by evaluating the ASP free energy at different temperatures.

3. Results and discussions

For Ni_7Ti_8Co supercell, the ASP degrees of atom Ni and atom Co on Ni site are defined as η_1 and η_2, respectively. The equilibrium lattice constants for $\eta_1 = 1$ and $\eta_2 = 1$, a_0, is determined as 0.3007 nm by the first principle total energy calculation, which is close to the experimental lattice constant of binary NiTi, 0.3014 nm [23]. At $\eta_1 = 1$ and $\eta_2 = -1$, the equilibrium lattice constants is just about 0.0002 nm different from a_0. The change of E_2 calculation resulted by lattice relaxation is less than 0.002 eV and can be neglected. Therefore, all the total energies of the supercells are calculated at a_0. The calculated total energies and the derived ASP energy coefficients are listed in Table 1. It can be seen from Table 1 that all the coefficients of the ASP energy are negative. Consequently, the ground atomic distribution state in the B2 phase of the concerned alloys should be $\eta_1 = 1$ and $\eta_2 = 1$. It means that the additional Co atoms prefer to occupy Ni sites, which agrees well with the experimental results [24].

In the Ni-poor region, the equilibrium atomic distribution state of the ternary NiTi–Co alloys at different temperatures can be determined by satisfying the following conditions,

$$\frac{\partial \Delta F}{\partial \eta_k} = 0 \quad (k = 1 \text{ and } 2) \quad (12)$$

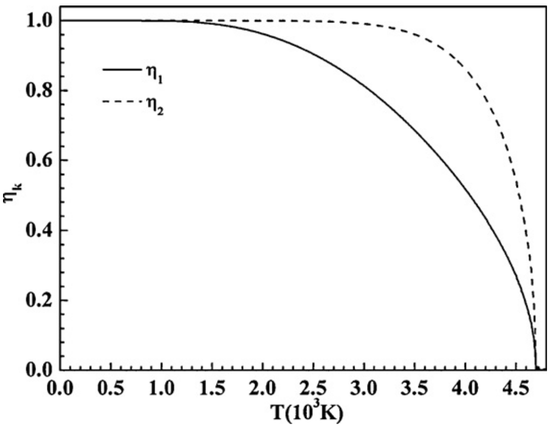

Fig. 2. Temperature dependences of the atomic site preference degrees for $Ni_{0.45}Ti_{0.5}Co_{0.05}$.

$$\frac{\partial^2 \Delta F}{\partial \eta_k^2} > 0 \quad (k = 1 \text{ and } 2) \tag{13}$$

and

$$\frac{\partial^2 \Delta F}{\partial \eta_1^2} \frac{\partial^2 \Delta F}{\partial \eta_2^2} > \left(\frac{\partial^2 \Delta F}{\partial \eta_1 \partial \eta_2} \right)^2 \tag{14}$$

Fig. 2 shows the temperature dependences of η_k for $Ni_{0.45}Ti_{0.5}Co_{0.05}$. According to the definition, η_1 denotes the coordination atom shift between Ni atom and Ti atom (atom shift procedure A), η_2 is for that between X atom and Ti atom (atom shift procedure B). The concentrations of anti-site Ni and Ti increase with the decreasing of η_1. By the decreasing of η_2, the concentrations of anti-site Ti can also be increased, and more X atoms located on Ti site are produced.

It can be seen from Fig. 2 that the atom shift procedure A occurs prior to the atom shift procedure B upon heating. The atom shift procedures A and B finish at almost the same temperature (about 4800 K). For $Ni_{0.45}Ti_{0.5}Co_{0.05}$, the B2 → bcc phase transformation temperature (order–disorder transformation temperature), T_c, is about 4800 K.

The additional atom concentration dependences of T_c for $Ni_{0.5-y}Ti_{0.5}Co_y$ are plotted in Fig. 3. It can be seen from Fig. 3 that the calculated T_c of the binary NiTi is about 3800 K, which is higher than the melting point of NiTi, T_m, 1583 K [25]. The same result of the calculated T_c being above T_m is also found in NiAl alloy [26], which just indicates that B2 phase is always stable up to T_m.

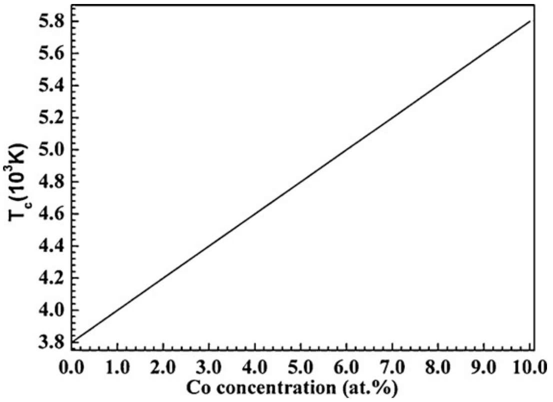

Fig. 3. Co concentration dependence of the order–disorder transformation temperature for the B2 phase of $Ni_{0.5-y}Ti_{0.5}Co_y$ ($y \geq 0$).

In general, T_c is one of the quantities to characterize the stability of the B2 phase. The higher T_c implies the higher stability of the B2 phase. The calculated T_c change by Co addition is about 200 K at.%$^{-1}$. It indicated that the B2 phase of the Ni-poor NiTi-based alloys should be more stable with more concentration of Co. It has been suggested that the enhanced B2 phase stability will suppress the B2 ↔ M transformation to lower temperature to reveal the B2 ↔ R transformation [4]. According to the changing rate of T_c, it can be expected qualitatively that the B2 ↔ M transformation temperature of the Ni-poor NiTi–Co alloys should be decreased monotonically by the increasing of Co concentration. When the Co concentration increases to a relatively high level, the overlapped transformation temperatures of B2 ↔ M and B2 ↔ R should be separated. Hence, the B2 ↔ R transformation can be provoked just in the case of the concerning NiTi-based alloys containing relatively large amount of Co addition. The qualitative deductions about the martensitic transformation of the concerned NiTi-based alloys agree well with the experimental results [8]: the changes of the start temperatures of martensite transformation of NiTi alloys by Co addition are −15 K mol%$^{-1}$ on the Ti rich side and −30 K mol%$^{-1}$ on the Ti poor side. Upon cooling, the B2 ↔ R transformation just occurs when the Co concentration increases to 6.0 at.%.

4. Conclusion

With the generalized atomic site preference model, the analytic expression of the atomic distribution state free energy of the third alloying additions in B2 binary alloys is obtained. Take advantage of the concentration independences of the configurational energy coefficients, a first principle calculation method of evaluating the configurational energy is developed. The first principle calculated order–disorder transformation temperatures of the B2 phase in the Ni-poor NiTi-based alloys change at the rate of about 200 K at.%$^{-1}$ by Co additions. The qualitative prediction about the effect of the third Co additions on the martensitic transformation procedure of the Ni-poor NiTi-based alloys is in good agreement with the experimental results.

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