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Composition-dependent elastic properties in TiNi-Nb from first principle calculations

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ABSTRACT

In this work, site-preference and elastic properties of TiNi-Nb austenite were investigated for various compositions, by using Exact Muffin-Tin Orbitals method in conjunction with Coherent Potential Approximation (EMTO-CPA). Moreover, composition-dependent elastic constants were calculated and used to explain the relation between composition and martensitic transition temperature. Our calculations suggested that Nb atoms prefer to occupy either Ni sites or Ti sites, depending strongly on composition. Variation of TiNi-Nb compositions is achieved through the formation of four sorts of defects: substituting Ti by Nb, substituting Ni by Nb, Ti anti-sites and Ni anti-sites. Our results suggested that c' increases when Ni is substituted by Nb, while c_{44} increases when Ni is substituted by Nb or Ni anti-sites form. Moreover, the maps of composition-dependent elastic constants were presented. TiNi-Nb with high c' and c_{44} could be obtained in Ni-deficient area. However, in Ni-excess area, only high c_{44} could be obtained. Changing of martensitic transition temperature is sensitive to the variation of c_{44}, rather than c'. With the variation of c_{44}, we explained the composition-dependent martensitic transition temperature for TiNi-Nb.

1. Introduction

TiNi shape memory alloys (SMAs) have been widely used in aeronautical and medical industry because of their shape memory properties and superelasticity. The relevant transition which is known as reversible martensitic transition is typically between high temperature cubic phase (B2) and low temperature monoclinic phase (B19′). Ternary TiNi-X SMAs are developed to further improve the performance and expand the application of this group of SMAs. Hf- and Zr-substituted TiNi alloys exhibit relative higher martensitic transition (MT) temperature, which is essential for high temperature applications. While Pt-substituted SMAs exhibit higher radiopacity [1]. Nb-substituted SMAs are attractive as fasteners and sealers. TiNi-Nb SMAs exhibit wider thermal hysteresis when deformed at low temperature, compared to unalloyed TiNi [2,3]. This is quite convenient in engineering application because wider thermal hysteresis enables deformed materials to be stored and transported at room temperature, rather than in liquid nitrogen. Apart from this, TiNi-Nb is supposed to exhibit superior damping capacity [4] and oxidation resistance [5]. To be a reliable fastener, there are two necessary conditions, relative low MT temperature and high yield strength [6]. These two conditions are closely related to elastic properties. Therefore, determination of composition-dependent elastic constants is essential for basic understanding and designing of TiNi-Nb SMAs.

1.1. Relations between elastic moduli and MT temperature

Elastic moduli of TiNi and TiNi-based alloys have been studied experimentally and theoretically. Elastic constants of TiNi alloys were firstly measured by Brill et al. [7] and Melton et al. [8] through ultrasonic experiments. Later, the crystal structure and elastic constants of TiNi were decided theoretically through Density Functional Theory (DFT) calculations by Ye et al. [9] and Sanati et al. [10]. The relations between MT temperature and elastic constants were investigated by Ren et al. [11–13]. They measured MT temperature and elastic constants c', c_{44} of TiNi austenite for different compositions and suggested that softening of elastic constants is a

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precursory phenomenon before MT. Elastic constant c'represents shear modulus of $\{110\}<1\bar{1}0>$ basal-plane shear, while c_{44} represents shear modulus of $\{001\}<100>$ and equal to that of $\{001\}<1\bar{1}0>$ non-basal-plane shear in cubic structure. Martensitic transition would arise from the softening of these two shear moduli. Conventional β-phase alloys (e.g. Cu-Al-Ni) exhibit large Zener anisotropy $A = c_{44}/c'(10-20)$. The large value suggests that $c'$is much smaller than c_{44} and that MT temperature is dominated by c' [12]. Experiments [14,15] indicates that martensitic transition occurs at almost constant values of c'. Slightly change in composition would cause strong deviation in the critical temperature at which c'softens to a critical value and martensitic transition occurs. This explains the strong composition-dependence of MT temperature. TiNi-based alloys exhibit low Zener anisotropy (~2). Therefore, formation of B19′martensite in TiNi alloys is associated with both $c'$and c_{44}. The hardening/softening of either elastic constants c'or c_{44} would alter MT temperature, depending on the hardening/softening rate [16].

1.2. Prior experimental and theoretical studies

It is now generally accepted that TiNi-Nb alloys are composed of TiNi matrix (with Nb solution) and Nb-rich precipitates [17–20]. Experiments were performed to investigate microstructure, martensitic transition mechanics, and mechanical properties for different compositions [21,22]. The relation between composition and MT temperature is continuously concerned in these experiments. On purpose that MT temperature could be controlled correctly. We can also find the relation theoretically through composition-dependent elastic constants. Composition-dependent elastic constants of TiNi and TiNi-based alloys were studied theoretically by Hu et al. [16,23,24] through EMTO-CPA method. Their work successfully explained composition-dependent MT temperature of off-stoichiometry TiNi and TiNi-X (X = V, Pt, Zr et al.). Unfortunately, TiNi-Nb was not included in their work. Moreover, composition-dependent properties of TiNi-Nb are more complicated because Nb atoms may substitute both Ni and Ti, compared with other previously investigated single-site-preferring situations. Only a few experimental or theoretical investigations have been performed to determine the composition-dependent elastic constants of TiNi-Nb. Shu et al. [25] investigated elastic constants of TiNi-Nb by using first-principles pseudopotential plane-wave method and indicated that Nb solution decreases both $c'$and c_{44}. However, they only calculated the elastic constants of TiNi-Nb for a single composition. Composition dependent elastic constants of this attractive material are still to be investigated. This paper is intended to investigate the composition-dependent elastic constants of TiNi-Nb and explain the composition-dependent MT temperature theoretically.

According to Ren et al. [11,12], elastic moduli are good indications of structure stability against shear distortion. Moreover, Shu et al. [25] suggested that Nb solution decreases $c'$and c_{44}, which indicates that Nb solution would increase MT temperature. Unfortunately, it seems that TiNi-Nb SMAs always exhibit lower MT temperatures when compared with unalloyed TiNi [2,17]. Therefore, further investigation of elastic constants of TiNi-Nb SMAs is essential to understand the influence of alloying element on MT. Elastic constants are dominated by electronic structure of solid systems. Therefore, first-principles electronic structure calculation is implemented in this paper to determine the composition dependence of elastic constants.

1.3. Overview of present work

In the present work, the exact muffin-tin orbitals method together with coherent potential approximation, being excellent in dealing with random alloys, are applied to investigate the composition-dependence of elastic moduli in TiNi-Nb matrix. This paper is arranged as follows. In section 2, we introduce briefly the computational method and key numerical details. Composition-dependent site-occupation and elastic properties are presented in section 3. The connection between calculated elastic constants and MT temperature is also discussed in this section. Finally, we conclude our work in section 4.

2. Computational methods

The high-temperature parent phase of nitinol is known as cubic B2, a CsCl-type structure. Elastic moduli $c'(=1/2(c_{11}-c_{12}))$ and c_{44} were investigated to study how alloying element influences MT. Before elastic moduli, the equilibrium volume V_0, equilibrium total energy and bulk modulus B_0 are determined firstly by fitting the total energy versus volume curve to exponential Morse-type function [26]. Single crystal elastic constants $c'$and c_{44} are derived from response of total energy to the volume conserving distortion of cubic cell at the equilibrium volume V_0. For the calculation of c_{44}, monoclinic distortion is applied according to

$$\begin{pmatrix} 1 & \delta_m & 0 \\ \delta_m & 1 & 0 \\ 0 & 0 & \dfrac{1}{1-\delta_m^2} \end{pmatrix}. \tag{1}$$

Total energies are fitted to monoclinic distortion δ_m as

$$\Delta E(\delta_m) = E(0) + 2Vc_{44}\delta_m^2. \tag{2}$$

For tetragonal shear elastic constant c', orthorhombic distortion is applied according to

$$\begin{pmatrix} 1+\delta_o & 0 & 0 \\ 0 & 1-\delta_o & 0 \\ 0 & 0 & \dfrac{1}{1-\delta_o^2} \end{pmatrix}. \tag{3}$$

Total energies are fitted to orthorhombic distortion δ_o as

$$\Delta E(\delta_o) = E(0) + 2Vc'\delta_o^2. \tag{4}$$

Total energies are calculated at equilibrium volume for $\delta = 0.00$, 0.01, 0.02, 0.03, 0.04, 0.05, respectively.

The EMTO method is based on the framework of density functional theory. It is an improved screened Korringa-Kohn-Rostoker (KKR) method [27–29]. Large overlapping muffin-tin spheres are used to describe crystal potential more accurately, compared to conventional muffin-tin approaches [30,31]. Full charge density (FCD) technique is implemented for total energy calculation which reproduces accurate total energies while maintain high efficiency simultaneously [30,32]. The implementation of CPA is supposed to reproduce reliable electronic structure for completely random alloy systems [33,34]. EMTO-CPA approach has been proved to be successful in the investigation of elastic properties of TiNi-based [23,24] and other randomly distributed alloys [35–40].

The one electron Kohn-Sham equation was treated with Green Function technique within scalar-relativistic and soft-core approximations. Our calculations included *s, p, d* and *f* orbitals in the EMTO basis set. Ten orbitals were used for the one center expansion of full charge density in the total energy calculation. According to Hu et al. [23], 16 complex energy points distributed exponentially