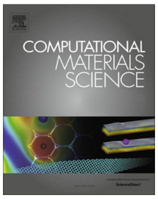
Computational Materials Science 112 (2016) 347–355

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci



Effect of ternary additions to structural properties of NiTi alloys

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ARTICLE INFO

Article history:
Received 14 April 2015
Received in revised form 23 October 2015
Accepted 24 October 2015

Keywords:
NiTi alloys
Ab-initio calculations
Ternary alloys
Structural properties

ABSTRACT

In this work, the effects of small ternary additions to B2 NiTi structures was investigated through DFT calculations. The analysis considered deviations from stoichiometry arising from either simple substitution of host atoms in a given sublattice or from the formation of anti-sites. The calculations enabled the determination of the site preference of X ternary additions. Moreover, the results suggest that ternary additions located in the central region of the transition metal group across all periods tend to occupy Ni sites due to favorable X–Ti nearest neighbor (NN) interactions. This occupancy is achieved through substitution or through the generation of anti-site defects. On the other hand, ternary additions at both ends of a given transition metal row tend to occupy Ti sites due to favorable X–Ni NN interactions. Once site preferences are determined, the effect of alloying on the thermodynamic and mechanical properties of B2 NiTi–X structures are presented and trends are discussed.

1. Introduction

Shape Memory Alloys (SMAs) exhibit the so-called shape memory effect (SME)—large reversible and macroscopic shape change triggered by temperature changes—and superelasticity (SME)—large recoverable strain triggered by mechanical stress—as a result of reversible thermoelastic martensitic transformations [1]. Owing to this behavior, SMAs (particularly those based on the Ni–Ti system) have become the material class of choice in the biomedical industry as they have enabled a wide range of biomedical equipment and devices in orthopedics, neurology, cardiology and interventional radiology [2]. In the case of NiTi-based SMAs, the relevant structural transition typically involves the transformation from a high temperature cubic austenite phase (B2-type) to a low symmetry monoclinic phase (B19′), although other martensite structures (such as the so-called R-phase) may be stabilized depending on the chemistry and microstructure of the austenite [3,4].

Further development of SMAs has been driven by the aerospace and automotive industries due to their potential as compact, reliable solid-state actuators [5]. More recently, the oil and gas industry has explored the use of SMAs [6] as couplers and fasteners. Unfortunately, usage of SMAs is limited by their typically low (below 100 °C) transformation temperatures. In the aerospace and automotive industries, in particular, design actuation temperatures are significantly higher than the operational limit of binary NiTi alloys [1]. Over the past decade, considerable effort has been invested in modifying the chemistry of NiTi-based SMAs (through ternary and quaternary substitutions of Ni and/or Ti) to increase transformation temperatures [7], control hysteresis [8], and/or improve mechanical properties such as strength and corrosion resistance [9].

1.1. Effects on martensitic transformation characteristics

There is already considerable experimental evidence for the dramatic effect of ternary additions on the martensitic transformation temperatures as well as phase transformation sequence in NiTi-based SMAs. Upon substitution of Ni by Cu at levels of about 10 at.%, a two-stage martensitic transformation is seen [10], where the cubic B2 austenite transforms first to orthorhombic B19, followed by a transformation to the monoclinic martensite B19′, contrary to the B2 → B19′ typically observed in NiTi. Upon additions above 10 at.% Cu, the transformation reverts to the conventional

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http://dx.doi.org/10.1016/j.commatsci.2015.10.029

single stage process. Addition of Cu also makes the martensitic start temperature (M_s) [11] and pseudoelastic hysteresis [12,13] less sensitive to composition changes and also prevents the precipitation of the metastable X-phase (Ni_4Ti_3) [13]. Finally, the transformation hysteresis associated with the B2-B19 transformation in NiTi–Cu is between those of the B2–B19′ and B2–R in Ni–Ti [12].

Replacement of small amounts of Ti by Zr in the NiTi alloy raises the M_s temperature in NiTi–Zr SMAs [14]. Mulder et al. [15] reported M_s temperatures above 120 °C in NiTi–Zr alloys for Zr content above 10 at.% and Ni content below 49.5 at.%. Addition of Ag to NiTi increases the austenitic transformation temperature (A_s). The NiTi–Ag alloys also showed higher martensitic phase fractions than several other NiTi based alloys.

Potapov et al. studied 8–20 at.% Hf, NiTi–Hf alloys fabricated by melt spinning, paying attention to the B19′ → B2 transformation at temperatures varying from 100 to 300 °C, and found that the lattice parameter of the parent B2 phase increases with Hf addition while the transformation volume almost remains constant. The transformation temperatures as well as the transformation temperature intervals between start and finish temperatures were found to increase [16]. Studies on rapidly solidified NiTi–Zr and NiTi–Hf SMAs have been performed using calorimetric and mechanical measurements, with emphasis on microstructural features and their influence on the martensitic transformation. The results show that in Zr- and Hf-substituted alloys the microstructure resulting from the rapid solidification conditions strongly effects the characteristic transformation temperatures. Higher solubility of the alloying components, and the present of coherent precipitates and other secondary phases lead to a significant decrease in M_s [17]. On the other hand, studies by Wojcik et al. shows that addition of Hafnium up to 10 at.% leads to increases in the transformation temperature by almost 100 °C [18].

One-way and two-way SME have been studied in DC-magnetron sputtered Ti–Ni, Ti–Ni–Pd and Ti–Pd thin films. Research showed that by substituting Ni with Pd the transition temperatures could be increased from 32–38 to 498–570 °C for Ti–Pd films [19]. Inter-diffusion of Ni and Si in NiTi thin films deposited on a silicon substrate and the resulting shape memory properties have been investigated and the resulting $Ni_xTi_ySi_z$ ternary alloys exhibited transition temperatures higher than NiTi SMAs [20].

The transformation behavior, shape memory effect and superelasticity of NiTi–V with equal substitution of V for both Ti and Ni have been studied and results show that adding 1–2 at.% V resulted in a slight drop (10 °C) in a single-stage B2 → B19′ martensitic transformation. Solid solution strengthening of NiTi SMAs by V improves their superelastic and shape memory response, although the formation of $(Ti,V)_2Ni$ second-phase particles within the NiTi–V matrix absorb oxygen atoms to form the $(Ti,V)_4Ni_2O$ oxide and in turn degrade the alloys' shape memory behavior [21].

1.2. Effects on performance

Up to 1.5 wt.% Ag increased the corrosion resistance of the alloys, but at higher silver levels the corrosion resistance showed a decrease [22]. Compressive strength is seen to improve dramatically at room temperature and higher temperatures by the substitution of Ti with Al [23]. This improvement in strength is partly due to the formation of Ni_2TiAl (Heusler compound) precipitate which is coherent with the NiTi(B2) matrix. In particular, researchers reported that an addition of 8.4 at.% Al showed an increase in compressive strength to 2400 MPa (at room temperature) and 250 MPa (at 1000 °C) comparable with mid-grade superalloys U500/U700 and Rene95 respectively. Experiments with Co addition show that substitution of Ni by Co in NiTi improves the yield stress and work hardening coefficient between room temperature and about 380 °C [24]. Moreover, addition of 1–2 at.% Co to NiTi increases the modulus, loading and unloading plateau by 30% as compared to the binary NiTi alloy [25].

Although not stated explicitly, studies suggest that the occupation of V on Ti sites yield a higher wear resistance, hardness and pseudoelastic behavior [21]. The ternary addition of Cr effects martensite transformation temperatures, M_s, as well as mechanical properties of off-stoichiometric NiTi alloys. M_s and A_s decrease with decreasing Ti concentration and change slightly when Ti concentration exceeds 52 at.%, where the alloys are in the two phase region. Significantly, M_s and A_s decreased with increasing Cr content at a constant Ti concentration. It was suggested that Cr atoms will substitute Ni sites preferably if only M_s changes are observed. Based on the characteristic stress–strain curves presented, the stress induced martensitic transformation (SIMT) occurred at −196 °C [24].

1.3. Effects on biocompatibility

Owing to their biocompatibility, NiTi-based SMAs are very useful in medical applications. SMA's have a high work output, which is necessary for minimally invasive instruments [26,27] and are superelastic, which makes them suitable for implants such as coronary stents [28]. Enhanced antibacterial properties, which can be achieved by addition of Ag, can significantly broaden their range of application. Silver is known for its antibacterial properties and Ag-alloy coatings are effectively used against a number of bacteria [29,30]. Moreover, addition of Ag also improves the corrosion resistance of NiTi SMAs which makes them suitable for orthodontic applications [22]. NiTi–Co are being considered for potential use since their superelasticity allows for durable, lower profile and less intrusive medical devices. NiTi–Co is also comparable to NiTi in terms of fatigue, corrosion resistance and biocompatibility. In NiTi–Mo alloys corrosion resistance can be improved by increasing an amount of Mo leading to improvement in biocompatibility [31].

1.4. Prior computational studies on NiTi–X alloying behavior

Bozzolo et al. [32,33] developed an approach based on quantum approximations, coined the Bozzolo–Ferrante–Smith (BFS) method, for analyzing SMA properties. In particular, Bozzolo focused on ternary bridge $Ni_{50-y}Ti_{50}X_y$ (i.e., where X = Fe, Pd, Pt, Au, Al, Cu, Zr, and Hf). The BFS method is based on the assumption that the energy of formation of a given atomic configuration can be quantified in terms of individual atomic contributions that account for lattice strain energy as well as chemical effects. The strain energy contribution can be obtained from the cohesive, structural and mechanical properties of the pure elements, while the chemical contribution accounts for the energetics of so-called pure and mixed bonds. In essence, the BFS method provides a very effective and computationally economical approach to investigate the energetics of alloying. One must point out, however, that this method is only indirectly related to first-principles calculations and some subtle bonding effects that cannot be simply separated into mechanical and chemical effects may not be captured.

In the case of their study of ternary X substitutions in NiTi, through the use of the BFS method, Bozzolo and collaborators were able to derive the lattice parameter, bulk modulus and energy of formation for the intermediate states in the (B2) transition NiTi to XTi. The substitutional elements considered through the BFS method in the work by Bozzolo and collaborators [32–34] were Au, Pt, Ir, Os, Re, W, Ta, Ag, Pd, Rh, Ru, Tc, Mo, Nb, Zr, Zn, Cu, Co, Fe, Mn, V, Sc, Si, Al and Mg. In a subsequent work by Mosca et al. [35], the BFS method was used to assess the behavior of ternary and quaternary additions to NiTi (i.e. ternary additions to NiTi and quaternary additions to NiTiPd, NiTiPt, and NiTiHf).