Journal of Alloys and Compounds 630 (2015) 54–59

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

First principles simulations of elastic properties of radiopaque NiTiPt

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ARTICLE INFO

Article history:
Received 2 October 2014
Received in revised form 8 December 2014
Accepted 10 December 2014
Available online 31 December 2014

Keywords:
Transition metal alloys
Crystal structure
Elasticity
Phase transitions
Computer simulations

ABSTRACT

Ternary NiTiPt is of great interest in the biomedical industry with the potential to replace binary NiTi in implanted devices due to the alloy's compatibility with medical imaging techniques and higher radiopacity. Cohesive and elastic properties are important for the processability and formability of materials using various hot and cold work methods. First principles simulations using density functional theory are reported here to determine the theoretical cohesive and elastic properties of NiTiPt with particular focus on nickel-rich stoichiometry. It has been found that Ni-rich NiTiPt alloy can form energetically stable cubic *B*2 phase, but only up to a platinum content of around 18.75 at.%. On the other hand, the titanium-rich composition can keep the *B*2 symmetry throughout the 0–50 at.% Pt range. Based on the observed trend in the elastic moduli cubic → orthorhombic → monoclinic phase transition has been suggested for both Ni-rich and Ti-rich compositions. With increasing platinum content the nickel-rich alloy becomes stiffer compared to the binary alloy. In contrast, the titanium-rich alloy exhibits a decrease in the Young's modulus as the platinum concentration increases. While both compositions suffer from elastic instability beyond certain amount of Pt addition, the ratio between the bulk modulus to the shear modulus indicates that they both should be reasonably ductile within the elastically stable range of Pt concentrations.

1. Introduction

Near equiatomic nickel-titanium alloy is popular in the biomedical industry owing to its excellent biocompatibility, high fatigue and corrosion resistance, shape memory (SM) and pseudoelastic properties [1–12]. The alloy has been used in wide range of implant applications such as stents and guidewires, orthopaedic screws, plates and surgical anchors [13,14]. Long-term implants or guiding devices made from NiTi alloy are often required to be visible under medical imaging techniques such as X-ray flouroscopy. The inherent poor visibility of NiTi is enhanced by adding radiopaque markers from elements possessing high radiation absorption coefficients, or by alloying those elements into NiTi. Elements such as W, Pd, Pt or some elements from the lanthanide group have been found to increase radiopacity of binary NiTi alloy and hence visibility under diagnostic imaging [15–17].

Alloying ternary elements into binary nickel-titanium affects temperature onset and finish for cubic austenite (*B2*) to monoclinic martensite (*B19′*) and reverse phase transformations. A stoichiometry change as low as 1% from near-equiatomic composition of NiTi has been found to drastically effect martensitic transformation (*MT*) temperatures such as those for martensite start and finish M_s, M_f, and austenite start and finish A_s, A_f [18–21]. Several authors reported this dramatic change in *MT* onset and finish temperatures with varying nickel content [19,22]. A decrease in M_s by ≈ 100 K within concentration range 50–50.8 at.% Ni has been found whereas almost no change has been observed on the titanium-rich side for less than 50 at.% Ni [19,23,24]. The amount of strain accommodated by the martensitic phase can also change with the stoichiometry and composition of the alloy [18,7,25,26].

Martensitic transformation in binary NiTi takes place through the rearrangement of atoms along a certain crystallographic direction from the parent austenite phase which is accompanied by the change in crystal structure [7]. Elastic moduli play an important role in the *MT*. Alloying with ternary elements is expected to further influence these properties as well as the austenite-to-martensite transformation path. A two stage transformation ($B2 \rightarrow B19 \rightarrow B19'$) through an intermediate orthorhombic phase has been observed in for example $Ni_{50-x}Ti_{50}Cu_x$ for $7.5 < x < 16$ at.% [7,27,28]. In the presence of more than 16 at.% of copper, the ternary alloy did not exhibit $B19 \rightarrow B19'$ transition and an orthorhombic *B*19 phase was the final transformation product [27]. There are alloy systems that exhibit different MT path through the intermediate trigonal *R-phase* as described by

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http://dx.doi.org/10.1016/j.jallcom.2014.12.185

Miyazaki et al. [29] and Shield and Hane [30]. The examples of such alloys include AuCd [31] and a number of NiTi based alloys [32–34,7].

Theoretical work on the stability of nickel-titanium alloys is in general agreement that the body-centred orthorhombic (*BCO*) phase is the ground state structure at the 0 K temperature [35,36]. The analysis of phonon-spectra of the austenitic phase however reveals that this CsCl-like structure is not stable due to negative (imaginary) branches at $M = [0.5, 0.5; 0]$ point in reciprocal space and there is another negative phonon mode present along $\Gamma \rightarrow R$ path. The negative phonon mode at M point generates a transformation to the orthorhombic phase that drives transition to a final $B19'$ martensite [37,38].

Elastic constants and transformation paths for binary NiTi alloy have been calculated and are generally in agreement with the experiment and consistent between different computational approaches used [18,39,40]. Elastic constants calculated for off-stoichiometric NiTi showed an increasing level of Zener elastic anisotropy in nickel-rich compositions, in contrast to a slight decrease in anisotropy when the titanium content increases [18]. Changes in the transformation temperatures in near-equiatomic nickel-titanium alloys, as documented in the literature [19,22,24], reflect a change in elastic constants of NiTi as a result of the off-stoichiometry. Molecular dynamics simulations with an increasing monoclinic angle have predicted the monoclinic angle to be more than 100 degrees, which in turn leads to an orthorhombic structure $B33$ [40]. This is in contrast with the experimental findings which report that the monoclinic angle in B19’ martensite is 97.8 deg. thus indicating that the monoclinic martensite is stabilized by the presence of internal stress [35].

The behaviour of defects in the binary system [41,42] as well as the site preference of ternary elements [43–46] in NiTi have been evaluated to understand the effects of such defects on elasticit and cohesive properties. Applications of binary nickel-titanium alloy in the micro and the nano industry, on the other hand, require low-dimensional structures to be explored. Recently, attention is being paid towards modelling and simulations of martensite transformation in these low-dimensional structures [47–50].

The addition of Pt significantly improves the radiopacity of binary NiTi [51] thus making ternary alloy attractive to potentially replace the use binary NiTi in biomedical industry. The common approach to ternary systems is to keep the alloy rich in titanium [52,46]. The nickel-rich stoichiometry has also been studied but with relatively less attention to its mechanical properties [53,51].

Cohesive forces and elastic constants are important determinants of the processability of an alloy. A fundamental understanding of the changes in these parameters due to the addition of Pt is therefore important. This motivates us towards using ab initio calculations within the density functional theory (*DFT*) framework to determine cohesive, structural and elastic properties of the nickel-rich ternary Ni(Ti,Pt) alloy for the first time. We compare these parameters with titanium-rich Ti(Ni,Pt) using same computational approach and available experimental data. Structural stability, MT transformation paths and temperatures are discussed with respect to the changes in elastic properties due to addition of Pt within the range of 0–25 at.%.

2. Computational details

Quantum mechanical calculations were performed on nickel-rich, Ni(Ti,Pt), using a plane-wave basis set and the projector augmented wave (*PAW*) technique as implemented in *Vienna ab initio simulation package* (VASP) [54]. The Perdew and Wang (*PW91*) parameterized generalised gradient approximation (*GGA*) functional was used for describing exchange and correlation [55,56]. Furthermore, we have used pseudopotentials treating $3d^8 4s^2$ orbitals for nickel, $3p^6 3d^3 4s^1$ for titanium and $5d^9 6s^1$ for platinum as valence states. The plane wave expansion energy cut-off was set to 430 eV and was kept constant throughout all calculations to allow for the basis set to adapt to the new geometry. For the Brillouin zone sampling, a k-point mesh was employed so that the separation of k-points in reciprocal space was 0.02/Å. This spacing in reciprocal space was kept constant for all investigated structures to keep the consistency between calculations. Methfessel and Paxton [57] scheme was used for the integration of the electron density within the Brillouin zone along with the smearing width so that the entropy contribution to the free energy was less than 1 meV per atom in a cell. Electronic loop was converged when the difference in energy of the electron density was less than 10^{-6} eV. The system was fully converged when forces acting on ions were less than 10^{-3} eV/Å.

Previous investigations on the site preference of ternary elements in nickel-titanium alloys revealed that the ternary elements tend to reside on the lattice site of the Ni or Ti, whichever is deficient from the stoichiometric amounts [43,44]. The creation of antisite and interstitial defects as well as vacancies has been found to be thermodynamically unfavourable. We adopt a similar approach to calculate the energetics of the solute element occupying titanium lattice site while keeping alloy rich in nickel. Furthermore, we kept the symmetry of the unit cell fixed to cubic $B2$ structure to explore ranges of Pt addition for which energetically and elastically stable structures can exist as $B2$ properties are crucial for austenite-to-martensite transformation.

The energy of formation, E_f, of defective structures was calculated from the total energy, E_0 at the equilibrium volume, V_0 according to the relation:

$$E_f = E_0 - \sum_i E_i \tag{1}$$

where $\sum_i E_i$ is the sum of the energy of respective constituents in binary and ternary alloys. The ground state total energy E_0 and the equilibrium volume V_0 were obtained by fitting the energy-volume dependence of cell volumes V within a range ±10% from the experimental value to the Murnaghan’s equation of state described by:

$$E(V) = E_0 + \frac{B_0 V}{B_0'} \left(\frac{\left(\frac{V_0}{V}\right)^{B_0'}}{B_0' - 1} + 1 \right) - \frac{B_0 V_0}{B_0' - 1} \tag{2}$$

From this equation, the bulk modulus B_0 at the equilibrium volume and its pressure derivative, B_0' were calculated as additional fitting parameters. For more than one Pt atom in a supercell, all symmetry non-equivalent configurations of dopant atoms were calculated and the structure with the lowest energy of formation was picked as a reference configuration for a given stoichiometry.

The calculation of elastic constants requires knowledge of the second derivatives of the energy with respect to the deformations represented by the strain matrix. Energetics of a deformed crystal has been analysed using strained orthogonal lattice vectors $a_i' = (1 + \varepsilon_{ij}) a_j$, where ε_{ij} is symmetric strain tensor with components $\varepsilon_i = (e_1, \ldots, e_6)$ in Voight’s notation and a_j is the unstrained lattice vector. The energy of the resulting strained state is given by:

$$E(\varepsilon_{ij}) = E_0 + \frac{V}{2} \cdot \sum_{i,j} c_{ij} \cdot e_i \cdot e_j \tag{3}$$

in which the term E_0 is the total energy of the unstrained crystal, the second term is the strain contribution to the total energy and c_{ij} is the 6×6 matrix of elastic constants. The elastic constant matrix is reduced to three elastic moduli c_{11}, c_{12} and c_{44} due to the symmetry constraints of the system. Conditions for the elastic