Theoretical investigation of the interaction of oxygen with pure and K-doped NiTi shape memory surface alloys

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Density functional based theories and experiments agree well on the value of the heat of formation of TiO₂ on NiTi surfaces. However, experimental studies of polycrystalline NiTi surfaces tend to indicate that Ti atoms are always abundantly available at the surface. This theoretical study indicates that whether Ti atoms are dominantly available at the surface depends on the surface index. On NiTi(001) in the B2 phase, the surface can be Ti or Ni terminated, with equal probability, while on NiTi(110) in the B2 phase and NiTi(010) in the B19' phase, Ti atoms are favored to be present at the surface.

1. Introduction

NiTi alloy with equiatomic composition (Ti – 50 at.% Ni) is known to be a shape memory material [1,2]. By application of force or temperature, it undergoes a change of structure from the parent austenite phase (B2) to the martensite phase (B19’) or vice versa [2]. If an impact is applied and released at one of the phases, the original shape would be recovered back at the other phase. The intermetallic composition is also being tailored for various purposes by varying the Ni content in the binary alloy or making a ternary alloy by replacing some of the Ni atoms with other transition metals [1,3]. However, this will typically lead to significant loss of the initial shape memory property. The alloy has also been confirmed to be biocompatible with body tissue and as a consequence it is being used in various medical applications including dentistry, orthopaedics, and vascular surgery [1,4,5].

The best biofunctionality of the alloy is achieved when the presence of Ni atoms at the surface layer is a minimum. This follows from numerous reports showing that high amounts of Ni atoms at the surface could result in a leakage to the body and cause hazards [6,7]. Appropriate surface treatment or coating is widely seen as the best remedy to this problem. Several studies have been devoted to quantitative characterization of surface oxidation [8,9] where a necessary amount of oxygen exposure to the surface was found to result in the formation of a TiO₂ protective layer [10]. In addition to increasing the corrosion resistance of the alloy surface [11], a TiO₂ layer is also believed to promote its biofunctionality [12]. However, it is not clear which surface index is the more reactive towards oxygen, and what is the corresponding relative stability of being terminated by Ti or Ni atoms prior to oxygen adsorption. To address these issues, this study makes an intensive investigation of (001), (110), and (111) surfaces in the B2 phase using density functional theory (DFT).

The B2 (austenite) phase has a CsCl type structure and exists at temperatures higher than about 330 K [13,14]. The B2 phase has also been found in several Ti based alloys [15,16] and even in NiTi based ternary alloys [17,18]. However, the B19’ phase with monoclinic structure is unique to the NiTi alloys and exists at temperatures lower than about 320 K. The B19’ (martensite) phase is sensitive to the composition of the alloy, and as a consequence, Ti and NiTi based alloys with different composition histories have different martensite transformation processes and martensite start temperatures (Mₛ) [8,13–15,17–19]. There is a lack of consensus on the position of atoms in the monoclinic unit cell in the literature [20,21] although the lattice parameters are all in good agreement. This inconsistency has been noted over the last few decades [22]. We have chosen the atomic positions described by Kulkova et al. [20] and considered the (010) surface for the oxygen adsorption study.

The (near) equiatomic NiTi alloy attracts attention because it undergoes the transformation with a change of structure from B2 to B19’ in just one step (i.e. with no other intermediate structure in between) [1,23]. Increasing the Ni content or alloying with a third transition metal by replacing some of the Ni atoms, extends the number of steps to at least two with an intermediate structure of rhombohedral (R) [18,19] or orthorhombic (B19’) [23] provided that the amount of Ni replacement is significant. When the amount of replacement is small, the transformation occurs in...
just one step where the $M_t$ temperature decreases slightly below 320 K, depending on the type of the added transition metal [24]. However, it is not clear what health impact these transition metals have when used in alloys in medical implants. Alkali metals (typically Na and K) when present in small amounts are known to be harmless for the body. They have been found to promote oxidation of semiconductor surfaces [25].

A recent experimental study [8] showed that the presence of a thin layer of K on the NiTi surface enhances the oxidation of surface Ti atoms to TiO$_2$. However, the impact of replacing some of the Ni atoms with K atoms is not clear. We will address this issue. The controlled replacement of Ni by K would likely decrease the $M_t$ temperature slightly, and importantly it is assumed to keep the transformation process simple (i.e. just one step). The main purpose of this report is to emphasize on the methodological approach. More extensive results can be found in [26].

The paper is organized as follows. In Section 2, details of the computational method are presented followed by the results and discussion in Section 3. We close the paper with some conclusions in Section 4.

2. Computational methods

2.1. Atomic orbital basis

For adsorbate coverage of 1.0–2.0 monolayers (ML), density functional theory based on the ADF/BAND program package [27] is used. A single electron approach based on the Kohn–Sham method is assumed and the electronic wave functions are considered as linear combinations of atomic orbitals [28]. The wave function of a core electron is approximated by the Herman–Skillman (HS) type numerical atomic orbitals (NAOs) [29] while that of a valence electron is approximated by one NAO (plus two Slater Type Orbitals) at each state, in what is called triple $\zeta$ quality. To allow for angular flexibility, two shells of higher angular momentum have been included in the basis set, i.e. triple $\zeta$ plus two polarization functions. Relativistic effects in its scalar form, as described elsewhere [30], have been taken care of in the kinetic energy of the electron, where it is calculated as

$$\frac{\hbar^2 \nabla^2}{2\mu}$$

$V$ being the total potential. The exchange and correlation effects are treated using Perdew and Wang (PW91) parametrization [31]. The density change upon the self consistent iterations is fitted by Slater type exponential functions and the corresponding density gradient has been used as a correction to the exchange correlation functional. The $k$ space integrations employed a tetrahedron method using irreducible $k$ points within the Brillouin zone [32].

The geometry optimizations are carried out based on the BFGS algorithm [33] where the elements of the Hessian matrix $H$ are updated as

$$\nabla E - \nabla E_{|r_0} = H_{ij} (r_i - r_0)$$

$E$ being the total energy of the system. Most of the geometry optimization calculations for the NiTi surfaces are performed with the spin unpolarized option. This is because our calculations did not show a clear preference for spin polarization treatment. Only energy differences up to 0.5 eV have been noticed, despite the expectation that Ni could pose a requirement for a polarization treatment. This is consistent with previous studies which have concluded that the NiTi systems do not reveal magnetic properties [21, 34].

2.2. Plane wave basis

For adsorbate coverages of 0.5–1.0 ML, a density functional theory based on the Dacapo code package [35] which implements Vanderbilt [36] ultrasoft pseudopotentials (VB) is used. A non-relativistic single electron approach based on the Kohn–Sham method is assumed. The calculations allow for spin polarization, and Ni atoms reveal a slight magnetic behavior with magnetic moments up to 0.72 $\mu_B$. Calculation of the total energy shows improvement by only about 0.06 eV when compared with spin restricted calculations, consistent with the prediction by method 2.1.

The purpose of using pseudopotentials is to replace the all electron (AE) interaction effects with an effective potential. As such, selected core electrons are considered part of an effective nucleus. Approximations of this kind are justified by the well-known fact that valence electrons dominate the chemical bonds. At the same time, the computational time compared to an AE approach is significantly reduced, making it possible to study larger systems in feasible time. A pseudopotential is significantly different from the AE potential within, say, a cutoff radius $r_c$, but generally converges to the AE potential outside $r_c$. The same applies to the corresponding wave function.

With the application of the Schrödinger equation to the $i$th state, this can be conveniently described as follows.

$$(T + V^{AE}) |\psi_i^{AE}\rangle = \epsilon_i |\psi_i^{AE}\rangle,$$

and

$$(T + V^{PP}) |\psi_i^{PP}\rangle = \epsilon_i^c |\psi_i^{PP}\rangle,$$

respectively, without or with use of pseudopotential. The extent to which energy eigenvalues ($\epsilon_i$ and $\epsilon_i^c$) and charges associated with the wave functions ($|\psi_i^{AE}\rangle$ and $|\psi_i^{PP}\rangle$) match are of importance for the transferability of the pseudopotential. Different pseudopotential implementations and frozen cores that exist today, including the VB [36] and HS [29] approaches, differ in their ability to recover these equalities.

As shown in Figs. 1(a) and 1(c), the eigenvalues calculated with the VB and HS approach are almost equal (Fig. 1(a)), but the values deviate by as much as 5.5 eV from the AE approach (Fig. 1(c)). The charge deviations are smaller, see Figs. 1(b) and 1(d), especially with the VB pseudopotential [36]. The extent to which these quantities are recovered differ slightly for the Ti and Ni atoms (see Figs. 1(a)–1(d)). This is a consequence of the cutoff radius used.$^1$ Upon calculation of energy differences such as adsorption energies, see Eq. (3), these differences are expected to be negligible. Note, however, that the nature of VB construction and its relatively larger cutoff radius$^2$ makes it require a relatively small basis set, enabling studies of large unit cells at a relatively low computational cost.

2.3. Surface models

The surfaces are modeled by a five layer slab where three layers are frozen at the bulk geometry while two layers are allowed to relax. The adsorbates are placed on one side of the slab and allowed to relax with the surface to obtain the optimum interaction geometry. The isolated adsorbate molecules were optimized in a cubic supercell structure with a unit cell size of 15 Å making sure that there is no interaction prior to adsorption. Oxygen is known to possess a triplet ground state in the gas phase, but it loses its spin polarization upon chemical interaction with a surface [37,38]. So, in this study, the adsorptive interaction process will be modeled by spin restricted geometry optimization.

$^1$ With ultrasoft pseudopotential, cutoff radius depends on the orbital and ranges as 1.8–2.0 a.u. for Ti atoms and 1.2–2.23 a.u. for Ni atoms. With HS method, the cutoff radii are 1.18 a.u. for Ti atoms and 1.23 a.u. for Ni atoms.

$^2$ See footnote 1.
The adsorption energy is calculated as

\[ E_{\text{ads}} = -(E_{\text{SA}} - E_{S} - E_{M}) \]

where \( E_{\text{SA}} \), \( E_{S} \), and \( E_{M} \) are total energies per unit cell calculated for geometries containing both the adsorbate and surface atoms, clean surface atoms, and isolated molecules, respectively. A positive \( E_{\text{ads}} \) implies an exothermic reaction. Adsorbate coverages are described in terms of the number of surface Ti atoms.

As shown in Fig. 2, both methods 2.1 and 2.2 consistently predict that in the B2 phase, NiTi(001) has the lowest total energy, followed by NiTi(110), followed by the NiTi(111) surface. The energy difference between the NiTi(001) and NiTi(110) is small, 0.29 eV by method 2.1 and 0.14 eV by method 2.2. However, it is significant between NiTi(001) and NiTi(111), 1.59 eV and 1.36 eV, respectively, by method 2.1 and method 2.2. A look at the favorability of atomic terminations indicates (not shown here) that the NiTi(111) surface is preferably terminated by Ni atoms. The energy of termination by Ti atoms is calculated to be about 0.29 eV higher with both methods. From this we assume that the NiTi(111) surface is not a good model candidate for interaction with oxygen. Similar calculations for NiTi(001) and NiTi(110) surfaces show that NiTi(001) has equal probability of being terminated by Ti or Ni atoms, while the NiTi(110) surface always terminates by Ti atoms. From the point of view of interaction with oxygen, the presence of Ti atoms at a surface is crucial. Meanwhile, noting the total energies of the surfaces, which implicitly indicate stabilities over different tem-
temperature ranges, we choose Ti terminated NiTi(001) and NiTi(110) surfaces to be good model candidates for interaction with oxygen. The surfaces at the B19' phase are all different because of low symmetry of its crystal structure. A similar calculation as above (not shown here) indicates that NiTi(010) has the lowest total energy, and always terminates by Ti atoms.

Theorems of finite temperature DFT have been continuously on the rise, from early times of ground state DFT [39] to the present [40]. However, the corresponding practical implementation for studies of periodic crystal systems is not widespread. There are several reasons for this. First, a study at finite temperature requires a calculation of grand canonical ensemble density \( \tilde{n}(r) \), which has the form

\[
\tilde{n}(r) = e^{-\beta G_i} \sum e^{-\beta G_i} \langle \phi_i | \phi_i \rangle.
\]

This makes it computationally expensive when compared with DFT studies at \( T = 0 \) K, where the corresponding calculation is an electron density \( n(r) \) which takes the form, say, \( \langle \psi_i | \psi_i \rangle \). For each state \( i \), the Gibbs free energy eigenvalue \( G_i \) takes the form \( G_i = \varepsilon_i - \mu N - TS_i \), which represents a tremendous effort when compared with the corresponding calculation of eigenvalues \( \varepsilon_i \) at \( T = 0 \) K. Second, unless inclusion of thermal effects is strictly required, some stability considerations can be made on the basis of calculations at \( T = 0 \) K. For example, it is reasonable to assume a higher value of entropy \( S_i \) in the B19' phase than in the B2 phase. On the other hand, a calculation at \( T = 0 \) K shows that total (electronic) energy is higher for B19' than B2. Hence, it can be argued that B2 should be a more stable structure than B19' at high temperatures. A similar analysis holds for various surface indexes too.

3. Results and discussion

The adsorption energy of oxygen with the chosen surface models is calculated to be in the range of 7.0–13.0 eV [26]. In comparison, the heat of formation of TiO\(_2\) on (poly)crystalline NiTi surfaces has been found to be about 9.9 eV [41,42]. The results are in good agreement, underscoring the quality of the models. At the same time, the results from the considered surface indexes, for example NiTi(001) at the B2 phase, is generalizable to other equivalent surface indexes such as NiTi(100), NiTi(010) of the B2 phase. Similarly, the case of NiTi(110) at the B2 phase can also be generalized to NiTi(011) and NiTi(101) at the B2 phase, and so forth. This understanding of equivalent geometries is of importance when comparing calculated results with experimental investigations on polycrystalline surfaces, which include diffraction data.

The two chosen surfaces of the B2 phase (NiTi(001) and NiTi(110)) offer different reactivities to oxygen, despite their sim-

![Fig. 3. (Color online.) Adsorption of oxygen on NiTi(001) at the B2 phase: (a) Top view of 1 ML of atomic oxygen adsorbed; (b) Side view of 1 ML of molecular oxygen adsorbed. Colors (size): Ti – green (large), Ni – grey (large), O – red (small).](image1)

![Fig. 4. (Color online.) Relaxations of surface Ti and Ni atoms of NiTi(001) at the B2 phase, upon adsorption of oxygen. \( \Delta z_0 \) – red (displacement of surface Ti atoms); \( \Delta z_0 \) – green (displacement of Ni atoms); \( \Delta d \) – blue (change of distance between surface Ti and Ni atoms); \( \Delta z_0 \) – magenta (displacement of Ti atoms after K doping).](image2)
ilar stabilities, see Fig. 2. For example, in Figs. 3(a) and 3(b), the coordinative adsorption site and initial growth of a TiO₂ oxide surface on NiTi(001) at the B2 phase is presented. The different initial growth patterns are ultimately of importance in limiting the minimum amount of TiO₂ layers required to grow on the surfaces before resuming a full protective role. The reader is requested to consult our recent publication [26] for an extensive presentation on this issue.

Analysis of the atomic positions shows that the interaction of adsorbate oxygen with the surface Ti atoms not only results in the formation of Ti oxides on the surface, but also depletes Ni atoms from the surface region, shown in Fig. 4. This is of particular importance as an application in biomedicine. Increasing the coverage of oxygen results in increased depletion (inward relaxation towards the bulk) of Ni atoms. The replacement of some of the surface Ni atoms by K, trivially depletes Ni atoms from the surface region. The understanding of such responses of the surface atoms to the adsorbates is crucial to a mechanistic design of quality biomaterials.

4. Conclusion

The obtained results are in line with what is sought for as an application to biomaterial. This reflects that the models are good representatives of the real material. The obtained insight on the relative displacements of the atoms is of importance for further studies and designs.

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References