Titanium $\alpha$-$\omega$ phase transformation pathway and a predicted metastable structure

N. A. Zarkevich and D. D. Johnson

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Titanium $\alpha - \omega$ phase transformation pathway and a predicted metastable structure

N. A. Zarkevich\textsuperscript{1} and D. D. Johnson\textsuperscript{1,2*}

\textsuperscript{1}Ames Laboratory, U.S. Department of Energy, Ames, Iowa 50011-3020 USA; and
\textsuperscript{2}Departments of Materials Science & Engineering and Physics, Iowa State University, Ames, Iowa 50011-2300 USA.

As titanium is a highly utilized metal for structural light-weighting, its phases, transformation pathways (transition states), and structures have scientific and industrial importance. Using a proper solid-state nudged elastic band (SS-NEB) method employing two climbing images (C2-NEB) combined with density-function theory (DFT+U) methods for accurate energetics, we detail the pressure-induced $\alpha$ (ductile) to $\omega$ (brittle) transformation at the coexistence pressure. We find two transition states along the minimal-enthalpy path (MEP) and discover a metastable body-centered orthorhombic (bco) structure, with stable phonons, a lower density than the endpoint phases, and decreasing stability with increasing pressure.

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I. INTRODUCTION

Titanium is one of the four (Fe, Cu, Al, Ti) most used structural metals and is the key component of strong, lightweight structural alloys used in aerospace, military, and automotive applications. Mapping competing phases and the associated phase transformations with stress (or pressure, $P$), temperature ($T$), and impurities can provide predictive design for improved control of alloy properties, including stabilizing metastable transition structures. For Ti at hydrostatic pressures above 2 GPa, the ground state hexagonal close-packed (hcp) $\alpha$-phase can transform into a brittle higher-density $\omega$-phase\textsuperscript{1-3} (Fig. 1). At high $P$, Ti transforms to denser phases: $\alpha \rightarrow \omega \rightarrow \gamma \rightarrow \delta$\textsuperscript{4,5}, while at high $T$ it transforms to the body-centered cubic (bcc) $\beta$-phase\textsuperscript{6,7}.

Previous theoretical investigations explored the transformation pathway – competing structures, minimum enthalpy pathway (MEP) and transition states (TS) – and some key results are in conflict with observations. For example, from experimental data\textsuperscript{1,6,8-15}, the $\alpha - \omega$ coexistence $P_0$ is 2 GPa determined from the inequality $P_{\omega \rightarrow \alpha} < P_0 < P_{\alpha \rightarrow \omega}$\textsuperscript{16}, valid for transformations between two solid anisotropic phases. At room temperature, the $\alpha \rightarrow \omega$ transition is observed from 2-15 GPa, depending on the pressure environment and sample purity. The $\omega \rightarrow \alpha$ transformation is observed below 2 GPa\textsuperscript{9}, but not for $P \geq 0$ for pure hydrostatic case with a gas, methanol-ethanol, or argon medium\textsuperscript{11}. Deviatoric anisotropic (uniaxial or shear) stress narrows the hysteresis\textsuperscript{9,11}. The recent theoretical $P_0$ of 5.7 GPa\textsuperscript{17} disagrees with experiment\textsuperscript{9}. In addition, Ti has strongly correlated $d$-electrons, and DFT returns inaccurate relative enthalpies of the groundstate and competing structures (e.g., hcp is not the lowest-energy structure at 0 GPa), with a calculated $P_0 < 0$ between $\alpha - \omega$ phases\textsuperscript{18,19}, which contradicts the experiments\textsuperscript{1-15}.

Here we revisit the pressure-induced Ti $\alpha - \omega$ transformation at the coexistence pressure. To detail the MEP and TS, we use the generalized solid-state nudged elastic band (SS-NEB) method\textsuperscript{20} based on DFT+U with onsite Hubbard corrections\textsuperscript{21} to support the required accurate relative structural enthalpies, atomic forces, and stress tensor for unit cells used for SS-NEB\textsuperscript{20}. Importantly, the SS-NEB method properly couples all atomic (or, using periodic unit cells, cell plus internal atomic) degrees of freedom and is mechanically consistent, including the MEP being invariant of cell size\textsuperscript{20}. Adjusting $(U - J)$ to 2.2 eV in DFT+U, we correct the inaccurate relative enthalpies and obtain the observed hcp ground-state at 0 GPa, and the observed coexistence pressure $P_0 = 2$ GPa; it is a value that reproduces the observed energy of reduction of Ti oxides (TiO$_2$ to Ti$_2$O$_3$), where 125 kJ/mol was matched by $(U - J) = 2.3 \pm 0.1$ eV\textsuperscript{22}.

Using SS-NEB combined with DFT+U, we find that the $\alpha - \omega$ transformation has two TS with a local enthalpy minimum, and discover a lower-density, body-centered orthorhombic (bco) metastable structure between them. This $\alpha \rightarrow$ bco $\rightarrow$ $\omega$ transformation can be considered as a sequence of two transformations. Impurities, pressure, and temperature control the phase stability and transition barriers in most industrial and geophysical materials – in Ti, interstitial O, N, or C retard while substitutional Al and V suppress the $\omega$ phase\textsuperscript{19}. The lower-density, bco metastable TS structure might be stabilized by impurities or negative stresses – potentially induced by chemical interstitial or substitutional alloying.

![FIG. 1: Enumerated 6-atom unit cells of $\alpha$ (hcp) and $\omega$ structures, suitable for the TAO-1 $\alpha - \omega$ transformation\textsuperscript{18}.](image-url)
II. METHODS

The $\alpha \rightarrow \omega$ transformation is considered in a 6-atom unit cell (Fig. 1). Applying the SS-NEB method,\textsuperscript{20} we detail the MEP (minimum enthalpy $H = E + PV$) and the transition states at coexistence pressure $P_0$ (Fig. 2), and versus applied pressures (Fig. 3). For accuracy, we use the C2NEB method,\textsuperscript{23,24} as tested on shape-memory transforms,\textsuperscript{25,26} to verify each TS. First, we turn off climbing and then sample the path by equidistant images. Next, one by one, each enthalpy maximum along the path is addressed by C2NEB. We fully relax each local enthalpy minimum and verify its stability. The details of the structure and electronic density (Fig. 4) and displacements and stress components (Fig. 5) are also provided for completeness.

We employ DFT+U with onsite Hubbard corrections,\textsuperscript{21} as implemented in VASP,\textsuperscript{27,28} using projector augmented waves (PAW)\textsuperscript{29,30} and PW91 exchange-correlation functional.\textsuperscript{31} For the 6-atom unit cell (Fig. 1), we use $12^3$ $k$-point mesh in the Brillouin zone, and a denser $24^3$ $k$-mesh for electronic density of states (DOS, see Fig. 6). Gaussian smearing with $\sigma = 0.05 \text{ eV}$ is used for relaxations; the tetrahedron method with Blöchl corrections\textsuperscript{32} is used for the final total-energy calculations. Atomic structures and data\textsuperscript{33} are visualized with VESTA\textsuperscript{34} and Grace software.\textsuperscript{35}

Phonons for the predicted bco structure are stable (Fig. 7); they are calculated via the small-displacement method.\textsuperscript{36} Details are given in section III.

III. RESULTS

Several mechanisms for the Ti $\alpha \rightarrow \omega$ transformation have been suggested.$^1$\textsuperscript{3,15,18} Previous DFT results\textsuperscript{18,19} found $\omega$-phase to be Ti groundstate at 0 GPa. In contrast, using DFT+U\textsuperscript{21} with $(U - J)$ adjusted to the experimental $P_0$ of 2 GPa – which matches the $(U - J)$ that also reproduces other Ti properties, such as the reduction energy of TiO$_2$ – we obtained, not so surprisingly, the hcp $\alpha$-Ti as the stable groundstate at ambient pressure, in agreement with experiment.

From SS-NEB and C2NEB calculations, we report the $\alpha \rightarrow \omega$ MEP at coexistence $P_0$ (Fig. 2), and MEP versus pressure (Fig. 3). Clearly, we find two TS, and, in between, we find a metastable intermediate structure ($m$), which is body-centered orthorhombic (bco). Hence, the $\alpha \rightarrow \omega$ MEP consists of $\alpha \rightarrow m$ and $m \rightarrow \omega$ transformations, with two barriers along the $\alpha \rightarrow m \rightarrow \omega$ path (18 meV and 16 meV, respectively). Recall that each nudged image in the SS-NEB attempts to be equidistant from its neigh-

![FIG. 2: Enthalpy (meV/atom) versus MEP at $P_0 = 2$ GPa, where $\alpha$ and $\omega$ enthalpies are equal within 0.15 meV/Ti. Dashed (red) line is volume $V$ (Å$^3$/atom) relative to $\omega$ (central scale), where $V(\omega)$ is 17.55 Å$^3$/Ti. Atomic motion within 6-atom cell is shown for hcp c-axis (top): dark (black) circles and light (blue) circles indicate two hcp sub-lattices.](image)

![FIG. 3: From SS-NEB (lines) and C2NEB (filled symbols), enthalpy (meV/atom) versus MEP at $P = 0$, 10, and 20 GPa. Change of volume (Å$^3$ per atom) relative to the $\alpha$-phase is given by dashed lines (right scale).](image)

![FIG. 4: 12-atom (conventional) unit cell of the metastable bco structure with layers of atoms (left), projected along $a$ (a), $b$ (b), and $c$ (c), where $a < b < c$. (d) iso-surfaces of electronic density (0.033 $e^–/Å^3$).](image)
bors along the MEP, and minimizes its enthalpy in all other directions within the NEB code.\textsuperscript{20,23,37} Hence, an enthalpy minimum along the MEP must be a local enthalpy minimum, i.e., a stable or metastable structure. Indeed, being fully relaxed, the local enthalpy minimum \( m \) (Fig. 4) does not transform to another structure, and, as expected, it has a stable phonon spectrum (Fig. 7). At low pressures, this bco structure has a lower density as expected, it has a stable phonon spectrum (Fig. 7).

At each pressure, we find two barriers in energy \( E \) for the \( \alpha \rightarrow \omega \) transformation. However, due to volume decrease along the MEP, the second barrier in enthalpy \( H = E + PV \) is suppressed at \( P > 10 \) GPa, see Fig. 3, so the stability of the bco structure decreases with pressure. In principle, this metastable intermediate structure during the \( \alpha \rightarrow \omega \) transformation can be determined experimentally by x-ray diffraction (XRD), as this process might be too fast for neutron scattering.

Note that the transformation generates significant anisotropic stress (Fig. 5). On the other hand, pressure anisotropy can facilitate the transformation. Indeed, an applied uniaxial or shear stress narrows the hysteresis in experiment.\textsuperscript{9,11} In fact, the reverse \( \omega \rightarrow \alpha \) transformation does not happen at \( P \geq 0 \) under hydrostatic conditions. As expected, anisotropic stress disappears at every equilibrium point, either stable (\( \alpha, m, \) and \( \omega \) structures) or unstable (both TS), see Fig. 5. During the transformation at \( P_0 \), the electronic DOS has a minimum near the Fermi energy, \( E_F \), for \( \alpha, m, \) and \( \omega \) structures (Fig. 6), as well as both TS configurations, which are the saddle points on the potential enthalpy hypersurface.

**Phonons of the metastable bco structure**

Phonons for the predicted bco structure are calculated via the small-displacement method, using the Phon code.\textsuperscript{36} At the \( \alpha \rightarrow \omega \) coexistence pressure (2 GPa), we displace each of the 6 atoms by 0.04 Å in three directions in the 162-atom \( 3 \times 3 \times 3 \) supercell of the bco cell. The calculated atomic forces (with subtracted forces of the relaxed structure) are used to construct the force-constant matrix, symmetrized for bco. The titanium atomic mass is

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\text{FIG. 6: DOS versus energy } E \text{ (relative to } E_F \text{) for Ti } \alpha, m, \text{ and } \omega \text{ phases at 2 GPa, with local minima at } E_F.\]

\[
\text{FIG. 7: Phonon frequencies and DOS in the metastable bco structure at 2 GPa (coexistence pressure).}\]
TABLE I: Direct coordinates of Ti atoms in the bco structure in terms of the translation vectors of the primitive 6-atom unit cell, $T_i = (-a/2, b/2, c/2)$; $T_2 = (a/2, -b/2, c/2)$; $T_3 = (a/2, b/2, -c/2)$, where the orthogonal lattice vectors at 2 GPa are $a = 5.02$, $b = 5.58$, $c = 7.63$ Å.

| $a$ | $b$ | $c$ (Å) | $v_0$ | $B_0$ | $B_0'$ | Method |
|-----|-----|---------|-------|-------|--------|--------|
| 2.972 | 4.728 | 18.09 | 111.7 | 3.6 | DFT+U |
| 2.9506(2) | 4.6795(4) | 17.64 | 109.3 | 3.355 | Expt. |
| 4.614(1) | 2.832(1) | 17.4 | 3.4 | DFT+U |
| m 5.052, 5.613 7.676 | 18.15 109.2 | 3.3 | DFT+U |

TABLE II: Lattice constants (Å) at 0 GPa and Birch-Murnaghan parameters $v_0$ (Å³/atom), $B_0$ (GPa), and $B_0'$ of the $\alpha$, $\omega$, and $\mu$ phases from DFT+U, neutron diffraction, and compressibility measurements.\textsuperscript{41}

Structural properties

The calculated structural parameters are given in Tables I and II. As expected, a positive Hubbard correction in DFT+U\textsuperscript{21} adds repulsion between electrons on the same $d$-orbital, which results in a slight increase of the lattice constants (which are 1% larger than in experiment) and atomic volume $v_0$, reported together with the bulk modulus $B_0$ and its pressure derivative $B_0'$ in Table II. These parameters were obtained by the least-squares fit of the Birch-Murnaghan equation of state to calculated volumes of the relaxed structures at hydrostatic pressure. The accuracy of the DFT+U methodology is well discussed in the literature.\textsuperscript{22,39,40}

IV. SUMMARY

We have detailed the pressure-induced Ti $\alpha - \omega$ transformation at the coexistence pressure via combined DFT+U\textsuperscript{21} and SS-NEB methods\textsuperscript{20,23}, using two climbing images in C2NEB\textsuperscript{23} for multiple transition states. With a judicious choice of $(U - J) = 2.2$ eV, DFT+U\textsuperscript{21} reproduces the observed coexistence pressure ($P_c = 2$ GPa) and the groundstate ($\alpha$ at $P < 2$ GPa) and provides correct relative structural enthalpies. It is not fortuitous that the same choice also reproduces well the reduction energies of Ti oxides\textsuperscript{22}. Importantly, we discovered a new metastable body-centered orthorhombic (bco) structure between two transition states (enthalpy barriers) along the minimal-enthalpy path. The predicted structure has stable phonons and a lower density than the $\alpha$ and $\omega$ end-point phases, but it has decreasing stability with increasing pressure (it is not stable above 10 GPa); it might be stabilized by impurities (under investigation), and provides an opportunity for engineering of lower-density titanium alloys, with additional strengthening by precipitation.

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