Research Article

Structural and Electronic Properties of Pure Ta, TaNO, and TaZrNO with Ab Initio Calculations

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This paper presents the results of self-consistent first-principle calculations for the crystal structure and electronic structure of pure tantalum, TaNO, and TaZrNO within density functional theory (DFT) for the sake of comparison and shows the influence of allowing elements on the interatomic distance and the Fermi level. The large total densities of states (TDOS) value for TaZrNO implies the highest electronic conductivity. The difference in values is due to the Zr metallic atoms presence in TaZrNO compound.

There is a strong interaction between Ta and (N, O) (Ta−N = 0.39, Ta−O = 0.21) in TaON compound, and Zr presence increases this interaction (Ta−N = 1.74, Ta−O = 0.30) in TaZrON compound.

1. Introduction

The elemental tantalum Ta crystallizes in three crystalline phases, bcc-Ta (α-phase), f.c.c-Ta, and a new phase which is now generally referred to as β-tantalum. The discoverers of the tetragonal tantalum β-Ta (a metastable phase), in 1965 are Read and Altman [1]. It has been attracting much interest in most applications because of its high resistivity (170–210 μΩ cm) [2–5]. It is preferred for fabricating capacitors and resistors. The chemical stability and robust mechanical properties of Ta make it a particularly desirable material. Numerous crystal structures have been reported for β-Ta. A tetragonal unit cell Ta was proposed by Read and Altman [1]. Das [6] proposed a bcc-based superlattice structure, while Burbank [7] proposed a hexagonal hcp structure and β-uranium model that was also proposed by Arakcheeva et al. [8, 9] on the basis of X-ray diffraction (XRD) study on single crystals of β-Ta produced through electrolytic crystallization, and in the end, the anomalous f.c.c-Ta structure was observed in very thin films of tantalum [10, 11].

On the other hand, nitride formation is common to most transition elements. Many compositional and structural forms exist, with many transition elements forming several different nitride phases. In many of these compounds, nitrogen atoms occupy interstitial lattice sites because they are smaller than the metal atoms. For this reason, they are often referred to as interstitial compounds. Transition metal nitrides are refractory metals that possess technologically useful properties including superconductivity and ultrahigh hardness, and they combine various physical and chemical properties, such as high melting points (around 3000°C). They also possess electronic and magnetic properties that make them useful as electronic and magnetic components and as superconductors [12].

Although monometallic nitrides have been the object of considerable studies [13–15], bimetallic transition metal nitrides have attracted only limited attention. Van Dover et al. [16] investigated the Ternary Transition-Metal Nitride Y-Nb-N and Gd-Cr-N Systems by reactive sputtering, providing evidence for a new superconducting (Nb,Y) N solid solution.

Similarly, the literature on oxynitrides has been scarce. Oxynitrides of transition metals are a new exciting class of materials [17] that possess interesting refractory behaviour,
higher elastic modulus, and hardness. They also offer great potential for their optical properties and recently have received much attention because of their potential use as pigment materials [18]. It has been known that oxygen atoms can substitute nitrogen atoms in monometallic nitrides due to the similarity in their radius. In many of the oxynitrides compounds, the N and O atoms are found in interstitial lattice positions in between the metal atoms. For this reason, their phases can exist over broad composition ranges with appreciable vacancy concentrations (both metal and nonmetal) and their physical properties are quite sensitive to composition. Yashima et al. [19] investigate neutron diffraction for confirmation of anion ordering and synchrotron powder diffraction for high-precision analysis of the crystal structure and electron density of an active TaON photocatalyst sample under visible-light excitation. Yashima et al. [20] employ the density functional theory (DFT) for theoretical calculations of the electron density distribution and partial density of states of TaON compound.

Our primary aim was therefore to present the results of a theoretical investigation of the structural and electronics of metastable β-Ta, bcc-Ta, and f.c.c-Ta. The bcc-Ta ((f.c.c-Ta)) structures are cubic; the space group is Im-3 m (no.229) (Fm-3 m (no.225)) with two (four) formula units per unit cell, the metastable β-Ta (β-uranium, Distorted A15, and Hexagonal) structures are (tetragonal P42/mnm (no.136), distorted Pm(-3)m (no.223), and hexagonal P63/mmc (no.194)). The bimetal (monometal) transition metal oxynitride TaZrNO (TaNO) structures are hexagonal (cubic), and the space group is P63m2 (no.187) (F43m (no.216)) with one (four) formula unit(s) per unit cell. Until now, there has been no report on the electronic properties of pure tantalum, TaNO, and TaZrNO.

This paper presents the results of self-consistent first-principles calculations for the crystal structure and electronic structure of pure tantalum, TaNO, and TaZrNO within DFT for the sake of comparison and shows the influence of allowing elements on the interatomic distance and the Fermi level.

The paper is organized as follows. The computational method is described in Section 2. In Section 3, the results are presented and compared with available experimental and theoretical data. Conclusion is given in Section 4.

2. Computational Method

All calculations were performed by using the CASTEP (Cambridge Serial Total Energy Package) simulation program [21] that solves the Schrodinger-like Kohn-Sham equations according to the formalism of the density functional theory (DFT) [22, 23]. We used the Generalized Gradient Approximation (GGA) and a Perdew-Burke-Ernzerhof (PBE) scheme [24] for handling the electronic exchange-correlation potential energy. Also, the pseudopotentials constructed using the ab initio norm conserving scheme describe the valence electron interaction with the atomic core, in which the Ta (4f14 5d5 6s2), Zr (4d2 5s2), N (2s2 2p3), and O (2s2 2p4) orbitals are treated as valence electrons. Using for all structures high cut-off energy (280 eV) even at the price of spending long computational time is the condition to obtain accurate results. Brillouin zone (BZ) sampling is carried out using a 6×6×6 Monkhorst-Pack mesh set [25]. For Ta (distorted A15) and hexagonal (type Cd or Zn) structures, the BZ sampling is carried out using a 10×10×6 Monkhorst-Pack mesh and a cut-off energy of (280 eV). Atomic positions are relaxed and optimized within a density mixing scheme, based on a Conjugate Gradient (CG) method for eigenvalues minimization. Actually, the equilibrium lattice parameter is determined from a structural optimization, using the Broyden-Fletcher-Goldfarb-Shенно (BFGS) minimization technique. This technique provides a fast way of finding the lowest energy structure, with the
following thresholds for converged structures: (i) energy change per atom less than $2 \times 10^{-5}$ eV, (ii) residual force less than 0.05 eV/Å, (iii) atom displacement during geometry optimization less than 0.002 Å, and (iv) maximum stress within 0.1 GPa. The crystal structures of Ta: β-uranium, Ta: Distorted A15 β-structure, and TaZrNO structure are given in (Figures 1, 2, and 3).

3. Results and Discussion

3.1. Structural Properties. Results for the lattice parameter $a$, $c$ and $c/a$ are reported (Table 1) and compared with experimental and theoretical calculations. Our calculated GGA values for $a$ for pure tantalum are in good agreement with the experimental data [1, 3, 7]. We have obtained the same value for $a$ of TaNO as experimental [26] one. For TaZrNO, our computed lattice constant ($a$) is bigger than the experimental one, within 7.4% [27]. Also, for both structures, the calculated lattice parameter ratio $c/a$ (0.523, 1.978, and 1.792 for 0020β-uranium, distorted A15, and hexagonal, resp.) is in reasonable accord with the previously considered data (0.531, 1.860, and 1.890, [1, 7, 28–31] and 1.098 for TaZrNO that is also in reasonable accord with of 1.064) [27]. In order to attempt an understanding the interatomic distances of the various compounds, we have found excellent agreement between our calculated...
peak, lying at and above $E_f$, has $d$ character with small admixture of $p$ characters and is responsible for the $N(E_f)$ of 26.024 and 18.268 states/eVÅ³ for $\beta$-uranium and distorted A15 models, respectively. For the hexagonal model, the DOS is primarily due to the $d$ states, with small $s$ characters at around $-5$ and $10$ eV (Figure 6). Figures 7 and 8 show respectively the density of states for $\alpha$-Ta and fcc-Ta that are mainly dominated by $d$ states and little $s$ contributions especially around $-5$ eV. Both structures are metallic because of the finite DOS at the Fermi level ($E_f$). The DOS values at $E_f$ of all structures are shown in Table 2. Let us mention a large DOS at the Fermi level, this implies a high electronic conductivity and various applications to electronic conductors. Figures 9 and 10 show the total density of states (TDOS) and partial density of states (PDOS) for TaNO and TaZrNO compounds. The TDOS of TaNO (TaZrNO) can be mainly distributed in the following three energy regions in the valence bonding region.

1. In the region one from approximately $-26$ eV to $-23$ eV ($-25$ eV to $-22$ eV). In this region, the DOS mainly consists of $s$ orbitals of O, together with a small portion of $s$ orbitals of Ta ($s$ orbitals of O, together with a small portion of $s$ orbitals of Ta and Zr). These states represent the electronic core structures;

2. In region two, it is from $-18.0$ eV to $-16.0$ eV ($-19$ eV to $-17$ eV). In this region, the DOS is contributed mainly from the hybridized $s$ orbitals of N, $d$ orbitals of Ta, together with a small portion of $s$ orbitals of Ta for TaNO, and the same behavior is observed for TaZrNO compounds;

3. In region three; it is from $-14$ eV to $0$ eV ($-12$ eV to $0$ eV). This is due to the $p$-O, $p$-N, and $d$-Ta orbitals ($p$-O, $p$-N, $d$-Ta, and $d$-Zr with a small portion of $s$-Ta and $s$-Zr contributions). Above the Fermi energy level, the DOS is predominated by $d$-Ta and $p$-N orbitals with a small portion of $p$-O contribution ($d$-Ta, $d$-Zr, $p$-N, and $p$-O orbitals with a small portion of $p$-Ta and $p$-Zr contributions), corresponding to the electronic anti-bonding states. The two TDOS have some similarities, however, in Figures 9 and 10.

TDOS at the Fermi level is 1.493 for TaNO.

TDOS at the Fermi level is 2.010 for TaZrNO, and the large value for TaZrNO implies the highest electronic conductivity.

The difference in values is due to the Zr metallic atoms presence in TaZrNO compound.

The pure tantalum has the highest ($E_f$), and generally speaking, the smaller the ($E_f$) is, the unstable the compound will be.

3.2.1. Bond Orders between Atoms. Bond order is the overlap population of electrons between atoms, and this is a measure of the strength of the covalent bond between atoms. If the overlap population is positive (+), a bonding-type interaction is operating between atom, whereas if it is negative (−), an antibonding-type interaction is dominant between

and available experiment interatomic distances for different phases of pure tantalum. The results of distances are reported in Table 1.
Figure 9: Total and partial densities of states for TaNO.

Figure 10: Total and partial densities of states for TaZrNO.
atoms. It is apparent that the bonding-type interactions are operating between the metal M (M = Ta, Zr) (4d and 5d) and the nonmetal (N, O) 3d electrons. Thus, there is a strong interaction between Ta and (N, O) (Ta − N = 0.39, Ta − O = 0.21) in TaON compound, and Zr presence increases this interaction (Ta − N = 1.74, Ta − O = 0.30) in TaZrON compound.

4. Summary and Conclusion

Using the first principles based on the DFT, we studied the total (partial) density of states TDOS (PDOS) of pure tantalum, TaNO, and TaZrNO. The large value for TaZrNO implies the highest electronic conductivity. The difference in values is due to the Zr metallic atoms presence in TaZrNO compound. A bonding-type interaction is operating between atoms, and thus there is a strong interaction between Ta and (N, O) (Ta − N = 0.39, Ta − O = 0.21) in TaON compound, and Zr presence increases this interaction (Ta − N = 1.74, Ta − O = 0.30) in TaZrON compound.

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| Materials       | Lattice constant $a_0$ (Å) | $c/a$ | Shortest Ta-Ta (Å) | Density (g/cm$^3$) | Atom/unit cell | Reference   |
|-----------------|---------------------------|-------|-------------------|-------------------|----------------|-------------|
| β-uranium       | 9.9345                    | 0.523 | 2.608             | 17.582            | 30             | [28, 29]    |
| Distorted A15   | 10.194                    | 0.531 | 2.650             | 16.330            | 30             | [1, 30, 31] |
| Hexagonal       | 5.1551                    | 1.978 | 2.550             | 17.736            | 16             | [7]         |
| α-Ta            | 5.3400                    | 1.860 | 1.890             | 16.960            | 16             | [7]         |
| TaNO            | 2.804                     | 1.792 | 2.805             | 17.605            | 2              | [7]         |
| f.c.c-Ta        | 2.830                     | 1.890 | 2.830             | 16.230            | 2              | [7]         |
| α-Ta            | 3.217                     | —     | 2.786             | 18.050            | 2              | [3]         |
| f.c.c-Ta        | 3.31                      | —     | 2.860             | 16.550            | 2              | [3]         |
| TaZrNO          | 4.108                     | —     | 2.905             | 17.329            | 4              | [4]         |
| TaZrNO          | 4.390                     | —     | 3.100             | 14.21             | 4              | [11–31]     |
| TaNO            | 4.827                     | —     | 3.031             | 17.978            | 12             | [26]        |
| TaZrNO          | 4.827                     | —     | 3.707             | 13.733            | 4              | [27]        |

| Materials       | Reference   |
|-----------------|-------------|
| Distorted A15   | [1, 30, 31] |
| Hexagonal       | [7]         |
| α-Ta            | [7]         |
| f.c.c-Ta        | [7]         |
| TaNO            | [26]        |
| TaZrNO          | [27]        |

Table 1: Lattice constant, shortest Ta-Ta, density, and atomic/unit cell of the all metastable phase.

| Materials       | β-uranium    | Distorted A15 | Hexagonal | α-Ta | f.c.c-Ta | TaNO | TaZrNO |
|-----------------|--------------|---------------|-----------|------|----------|------|--------|
|                | 26.272       | 18.268        | 2.418     | 2.579| 4.704    | 1.493| 2.010  |

Table 2: Fermi level $E_f$ of the all metastable phase.
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