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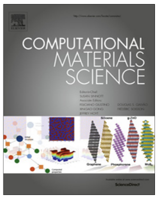

Ab initio investigations of the phase stability in group IVB and VB transition metal nitrides

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ABSTRACT

Using a combination of electronic structure density functional theory and an evolutionary algorithm, we predicted the thermodynamically stable structures of the group IVB and VB transition metal nitrides at 0 K. Our results demonstrate that in the group IVB nitrides there is a competition between nitrogen interstitial ordered forms of the hexagonal close packed structure and nitrogen vacancy ordered forms of the B1 structure. The low metal vacancy formation energies in the B1 structure even allowed metal vacancy ordered forms of the B1 HfN structure to be thermodynamically stable. The work also revealed how bond distortion and bond angles allowed the predicted Ti_2N and Zr_2N $P4/mnm$ phases to be stable as compared to the $Pnnm$ structure for Hf_2N. This work also predicted several metal-rich phases to be present in the Zr-N system, which have yet to be observed potentially owing to this system being the least experimentally studied of the group IVB nitrides. In the group VB nitrides, the low formation enthalpies of the ε-TaN prototype and B_h structures, as well as the C6 structure, suppress the dominance of the B1 phase at low temperatures. The collective results provide in-depth and inclusive examination of the similarities and differences for phase stability in these two classes of transitional metal nitrides at 0 K.

1. Introduction

Transition metal nitrides comprise a class of high and ultrahigh melting temperature ceramics that have found a variety of uses from electrical insulators for microelectronic devices to hard coatings in cutting tools as well as potential structural components in next-generation, hypersonic vehicle applications [1–7]. This range of uses is attributed to the diverse set of properties that are derived from their crystal structures and their microstructures. Transition metal nitrides, depending on the nitrogen stoichiometry, can form a variety of single and multiphase constituents with the metal-rich phases having different bonding characteristics than their mononitride counterpart [8–15]. These particular nitrogen-lean phases tend to have reduced crystallographic symmetry as well as differences in nearest neighbor atomic alignments, including metal-metal and metal-nitride bonds within the same unit cell. Such characteristics generate complications in electronic transfer (bonding) that results in a variety of potential phases and unique sets of mechanical, optical, and electrical properties. Elucidating the stability of these phases is then essential for systematic engineering development.

In a recent computational paper by Yu et al. [16,17] on the phase stability of transition metal carbides, a competition between stacking fault and vacancy ordered phases was noted with ever depleting carbon content. This resulted in a variety of metastable phases to form. One of these phases is the rhombohedral zeta-Ta_4C_3 phase, which in large volume fractions, has been shown to significantly increase the fracture toughness [18–20]. Through the computational work, an intrinsic stacking fault (ISF) was found in the group VB transition metal carbides and is believed to help facilitate the faulted nature of this phase's precipitation [21]. This ISF has even been shown to regulate the slip between transition metal carbides [22]. This ISF, and the accompany zeta phase, is absent in group IVB transition metal carbides even though both stoichiometric carbides stabilize the rock-salt structure with approximately equivalent melting temperatures (suggesting similar bonding behavior). Unlike these group IVB transition metal carbides, the group IVB transition metal nitrides are reported to have comparable faulted crystallographic phases as the group VB carbides [23,24] which has facilitated the need for this computational study to better understand the nitrides phase stability.

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Of the group IVB transition metal nitrides, and in particular the hafnium nitrides, there has been debate on the stability of the faulted phases. In the original work by Rudy and Nowotny [25], a hexagonal-based Hf_2N structure was reported; however, it was later corrected to be two types of rhombohedral phases being ζ-Hf_4N_3 and η-Hf_3N_2 [23]. Even more intriguing is that in nitrogen-rich hafnium nitrides, a stable Hf_3N_4 phase has been observed [26–29], which is an absent phase in the carbides. Similar to the nitrogen lean phases, some controversy has existed in terms of this nitrogen-rich phase's exact crystallography, whether it being the Th_3P_4-type ($I\bar{4}3d$) [29], the tetragonal $I4/m$, or $Pnma$ structures [30–32]. In large part, the discrepancy of the crystal structure likely resides in how this particular transparent semiconductor was processed - by thin film deposition or under a heated diamond anvil. In a recent computational report by Zhang et al. [33], the phase stability of the hafnium nitrides under pressure was discussed in detail. In their research, they reported a series of vacancy ordered interstitial phases in the hafnium-rich nitrides. They also noted that the mono-hafnium nitride's thermodynamically lowest temperature phase was $P6_3/mmc$ and not the B1 rocksalt structure, with the latter being commonly observed experimentally. These types of computational driven insights, very much like the computational carbide work, leads to a further and more complete understanding of the stability of non-metal species ordering within metal crystal lattices.

Besides the hafnium nitride work by Zhang et al. [33], computational studies in other nitride systems have been undertaken. Notably, Yu et al. [34] have studied the Ti-N system and found the ε-Ti_2N and δ-TiN structures being stable along with Ti_3N_2, Ti_4N_3 and Ti_6N_5 phases present on the convex hull. There have been two notable studies on the tantalum nitride phase system [35,36] which have substantial differences in the identified phases that lie on their convex hulls. Part of the confusion resides in the oft incorrectly identified form of ε-TaN [37–41], which has been a decade's old problem that continues to create issues in appropriately constructing the convex hull. In this paper, we will further elaborate on this discussion in terms of our findings below.

Thus, this work has aimed to further the computational efforts in the group IVB and VB transition metal nitrides. As evident in the prior discussion, several of these phases' stability have not been concretely determined where in other systems some debate still exists. Furthermore most of the prior studies aimed at single system investigations making comparisons within and between transition metal groups more arduous or even incomplete. By performing studies across these two transition metal nitride families, a more holistic study has been provided where self-contained comparisons can be drawn and new insights into phase stability gained.

2. Computational methodology

The approach we have taken is similar to our previous work [16] on the transition metal carbides in that we start with an evolutionary algorithm to determine the crystal structure for all 6 group IVB and VB transition metal nitrides. The use of an evolutionary algorithm removed part of the bias, and potential mistakes associated with that bias, to determine the ground state structures.

To this end, we utilized the USPEX code to run an evolutionary algorithm [42,43]. The code performed a global optimization using real-space representation and physical variation operators. For each structure selected by the algorithm, the structures and atomic position were relaxed at 0 K using the Vienna Ab-initio Simulation Package (VASP) using a plane wave basis [44,45]. The core electrons were treated using PAW pseudopotentials [46,47] while the outermost electrons were treated explicitly in the code. The exchange correlation energies were approximated with the generalized gradient approximation (GGA) using the parameterization of Perdew Burke and Ernzerhoff [48]. Plane waves with a cut-of energy of 600 eV and k-point mesh resolution in reciprocal space of $2\pi \times 0.03$ Å^{-1} yielded converged results.

The search executed in the USPEX code utilized 30 atoms per unit cell with 50 structures selected at random in the first generation. All other generations contained 40 structures, 40% were produced from heredity, 20% by soft mutation, 20% by transmutation and 20% randomly. The calculation was terminated after the stable structures did not change for at least 10 generations, but at least 40 generations were run for each system.

Once the evolutionary algorithms were completed for each system, all of the low energy structures were catalogued and combined with known structures from the database that was constructed from the nitrides and re-run for each system. This was then used to construct the convex hull of the enthalpies of formation for each nitride system.

3. Results and discussions

3.1. Convex hull results

For the titanium nitrogen system, the equilibrium phases at 0 K are plotted on the convex hull in Fig. 1(a) and have been identified as the following: the B1 structured TiN phase, the Ti_6N_5 ($P3_1$), Ti_4N_3 ($C2/c$), Ti_3N_2 ($Immm$), and ε-Ti_2N ($P4/mnm$) phases. These have also been tabulated in Table 1 and a complete list of all structures in Fig. 1 are listed in Tables A1 and A2. We note that previous work predicted nearly the same equilibrium phases for the Ti-N system [34], though, we have now identified a slightly lower energy form for the Ti_4N_3 compound. The prior report indicated that the lowest energy structure belonged to the $C2/m$ space group where we have identified the lowest state to belong to the $C2/c$ space group. It is important to note that the energy difference between these structures is approximately 0.005 eV per atom, quite a small value, and one can imagine with entropic effects the stability could oscillate the stable structure between either phase. We further noted that the Ti_3N_2, Ti_4N_3 and Ti_6N_5 structures are all vacancy ordered forms of the B1 structure, a behavior that has been commonly predicted to occur in the carbides [16,49], as well as in the limited number of nitride computational investigations [33,34].

For the zirconium nitrogen system, with the convex hull plotted in Fig. 1(b), the equilibrium phases at 0 K are the hexagonal ZrN ($P6_3/mmc$), Zr_6N_5 ($P3_1$), Zr_4N_3 ($C2/m$), Zr_2N (the ε-Ti_2N structure or $P4/mnm$), and the Zr_7N_8 ($P\bar{1}$) phases. These are listed in Table 2. The emergence of the newly reported hexagonal HfN structure, with space group $P6_3/mmc$ as the 0 K stable structure [33], was confirmed in these findings to be present for ZrN as well. In the metal-rich composition, we again discover that the equilibrium structures are similar to those of the Ti-N system, as one could potentially predict since both metals (Ti and Zr) are from the same group IVB transition metal family. Though subtle differences are found. For example, the ordering of the nitrogen atoms is different at the M_4N_3 composition with the Zr_4N_3 structure having a $C2/m$ space group while the Ti_4N_3 has a space group $C2/c$. And, in addition, the Zr-N system has a new stable phase – Zr_7N_8 – in the nitrogen-rich regime that was not present in the titanium nitrides. This phase is a zirconium vacancy ordered form of the rocksalt structure.

The convex hull for the hafnium nitrogen system, Fig. 1(c), identified the stable structures to be the hexagonal HfN structure ($P6_3/mmc$), ζ-Hf_4N_3 ($R\bar{3}m$), η-Hf_3N_2 ($R\bar{3}m$), Hf_2N ($Pnnm$), Hf_3N (P622), Hf_6N ($R\bar{3}$), and Hf_8N_1 ($C2/m$) for the metal rich compositions, listed in Table 3, with the zeta and eta phases known to be stable from