



Designing thin film materials – Ternary borides from first principles

H. Euchner ^{*}, P.H. Mayrhofer

Institute of Materials Science and Technology, Vienna University of Technology, 1040 Vienna, Austria



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ABSTRACT

Exploiting the mechanisms responsible for the exceptional properties of aluminum based nitride coatings, we apply ab initio calculations to develop a recipe for designing functional thin film materials based on ternary diborides. The combination of binary diborides, preferring different structure types, results in supersaturated metastable ternary systems with potential for phase transformation induced effects. For the exemplary cases of $M_xW_{1-x}B_2$ (with $M = Al, Ti, V$) we show by detailed ab initio calculations that the respective ternary solid solutions are likely to be experimentally accessible by modern depositions techniques.

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1. Introduction

The increasing demand in industrial applications calls for new protective coatings with high hardness, good elastic properties and improved ductility. Transition metal (TM) nitrides have proven to fulfill these requirements for different kinds of applications like automotive or aerospace industries. Nevertheless, the search for improved materials is an ongoing topic being far from its end.

It is well studied that the face centered $Ti_{1-x}Al_xN$ (B1 structure, rocksalt NaCl prototype), being the basis of many hard coatings [1], is a supersaturated structure and tends to decompose into the stable constituents, cubic TiN (B1) and hexagonal AlN (B4 structure, wurtzite ZnS prototype) [2,3]. The ability of $Ti_{1-x}Al_xN$ to crystallize in a single phase cubic structure, when synthesized by vapor phase deposition techniques [4] allows combining several advantages. The cubic phase has superior physical and mechanical properties like hardness and elastic moduli as compared to the wurtzite structure. Additionally, with increasing Al content, the oxidation resistance is strongly improved [1]. Moreover, with higher Al content, the supersaturation of the TiN-based cubic structure increases, which allows for self-hardening effect at elevated temperatures, resulting from the formation of TiN- and AlN-rich cubic domains [5,2,3]. Finally the transition from cubic to wurtzite AlN, which takes place upon further annealing or exposure to elevated temperatures, which typically results in a loss of mechanical properties, may yield a phase transformation induced toughening effect for controlled AlN phase fractions [6]. The

latter is based on the enormous 26% volume increase upon transformation from the metastable cubic to the stable hexagonal structure. Consequently, it can be concluded that the unique properties of $Ti_{1-x}Al_xN$ originate from the interplay and competition between two phases that prefer different structure types – cubic TiN and wurtzite AlN.

Boron on the other hand is one of the hardest materials known. Therefore, a promising pathway to achieve strong materials with exceptional properties is the investigation of borides, which have attracted increasing interest in recent years. However, while ternary and even quaternary transition metal (TM) nitrides have been investigated in detail, borides and especially multinary borides are still rather unexplored. Consequently, we present first theoretical predictions for the development of single-phased ternary TM-diborides. These predictions are based on the well-studied mechanisms which are responsible for the exceptional properties of supersaturated cubic-structured $Ti_{1-x}Al_xN$.

A large number of diborides, including the early transition metal (TM) diborides, crystallize in the so-called AlB_2 structure type [7] with space group 191 ($P6/mmm$) and three atoms per hexagonal unit cell. In addition to the unit cell description it is instructive to represent the structure as a stacking of hexagonal planes of covalently bonded boron atoms, separated by the metal layers, as depicted in Fig. 1. While the boron layers consist of graphite-like hexagons, the metal atoms are located above (and below) the centers of these hexagons. Despite the fact that the AlB_2 structure type is the predominant one, there also exist diboride phases which prefer to crystallize in other modifications. One such phase is WB_2 , for which two structural modifications are reported [8–10]. While, recently thin films of WB_2 have been reported to crystallize in the AlB_2 structure type, bulk material seems

* Corresponding author at: Getreidemarkt 9, 1160 Vienna, Austria. Tel.: +43 1 58801 30843; fax: +43 1 58801 30895.

E-mail address: holger.euchner@tuwien.ac.at (H. Euchner).

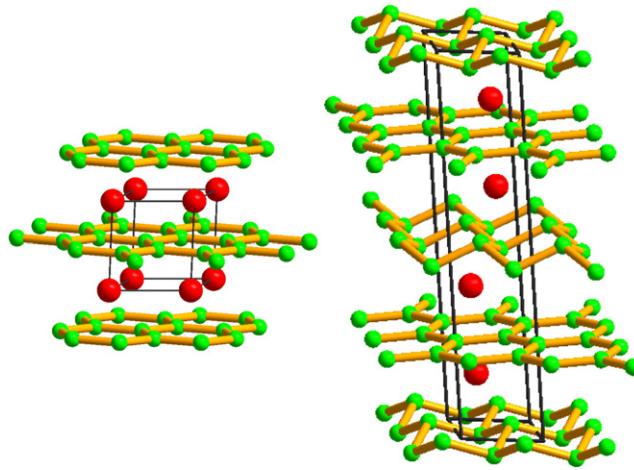


Fig. 1. Layer structure of AlB₂ (left) and WB₂ (right) prototypes.

to prefer the WB₂ structure type, formerly known as W₂B₅. The WB₂ structure type is closely related to the AlB₂ prototype but evidences a different layer structure. In fact, WB₂ consists of both flat and puckered boron layers, resulting in a twelve atom unit cell with space group 194 (P63/mmc) as depicted in Fig. 1.

Due to the existence of the different structural modifications, combining AlB₂-structured TM-diborides with WB₂ will lead to ternary model systems that are based on competing allotropes. In the following, three examples of such ternary model systems will be discussed with respect to formation and stability. As mentioned above, for WB₂ both, the AlB₂ (WB₂-191) and WB₂ prototype (WB₂-194) are reported. [8–10]. To distinguish these structural modifications, we use *a* and *w* to represent the AlB₂ (*a*-M_xW_{1-x}B₂) and the WB₂ prototype (*w*-M_xW_{1-x}B₂), respectively.

2. Computational methods

To investigate the respective stability of different metal diborides, MB₂ (with M = Al, Ti, V) and WB₂ in the *a*- and *w*-modifications, density functional theory (DFT) calculations have been conducted. The Vienna Ab Initio Simulation Package (VASP) [11–13] was used to optimize the respective structures, applying the projector augmented wave method within the generalized gradient approximation (PAW-GGA). The calculated total energies of the respective allotropes are denoted in Table 1. As expected *a*-MB₂ exhibits a more negative total energy than *w*-MB₂, whereas for WB₂ the opposite is true, meaning the total energy of *w*-WB₂ is more negative. Thus, as previously discussed in literature [14] we also find WB₂ to be energetically more stable in the WB₂ structure type, while MB₂ is stable in the AlB₂ structure type.

The absolute values of the energy differences between the *a*- and *w*-allotropes of AlB₂, TiB₂, VB₂, and WB₂ are of about 113, 390, 94, and 260 meV/at, respectively, which is in the same range as for the wurtzite and cubic modification of AlN. Moreover, a volume increase of about 6.5–9.5% is evidenced for the allotropic transformation of *a*-MB₂ to *w*-MB₂, which may be relevant for increasing fracture toughness. As a

consequence M_xW_{1-x}B₂ alloys are promising candidates for more detailed studies.

For an investigation of ternary M_xW_{1-x}B₂ phases, supercell structures of both structural modifications were constructed. In the case of *a*-M_xW_{1-x}B₂ a 4 × 4 × 2 supercell with 96 atoms was investigated, while for *w*-M_xW_{1-x}B₂ a 4 × 2 × 1 supercell, again containing 96 atoms, was selected. The respective metal sublattices were then populated by different M/W contents, making use of the special quasirandom structure (SQS) approach [15,16]. The obtained SQS structures were then optimized by means of DFT, applying an energy cutoff of 600 eV and a 4 × 4 × 8 Γ-centered k-point mesh for *a*-M_xW_{1-x}B₂, whereas in the case of *w*-M_xW_{1-x}B₂ a corresponding 8 × 4 × 4 k-point mesh was used. Energy cutoff and k-point mesh were carefully chosen to ensure energy convergence within an accuracy of about 1 meV/at.

3. Results and discussion

To determine the respective stability of both structural modifications of M_xW_{1-x}B₂ at a given metal concentration, the energy of formation, E_f, was calculated following Eq. (1):

$$E_f = \frac{1}{\sum_i n_i} (E_{\text{tot}} - \sum_i n_i E_i) \quad (1)$$

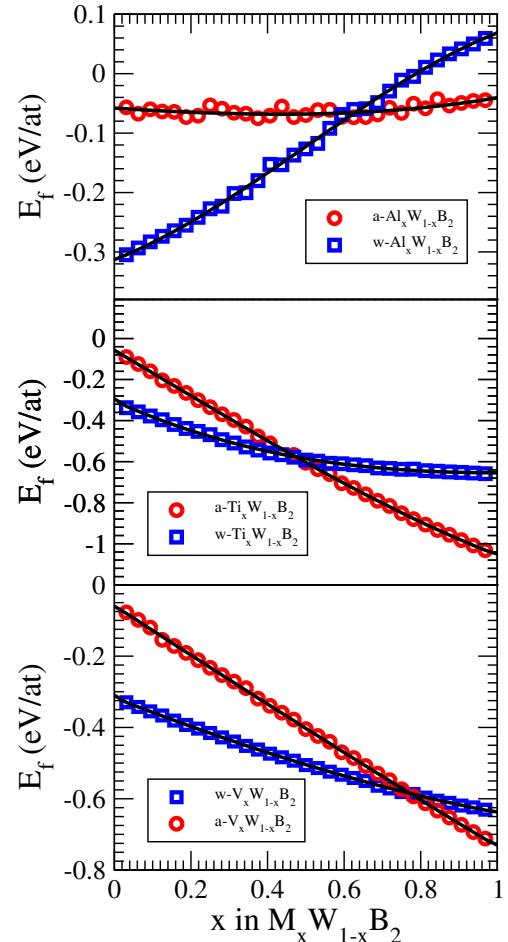


Fig. 2. Energy of formation of M_xW_{1-x}B₂ in the respective allotropic modification (red circles: *a*-M_xW_{1-x}B₂, blue squares: *w*-M_xW_{1-x}B₂). The black curves are fits to the data.

Table 1
Total energies for MB₂ and WB₂ in the respective allotropic modification.

Structure type	AlB ₂		WB ₂	
	E _{tot} (eV/at)	Vol (Å ³ /at)	E _{tot} (eV/at)	Vol (Å ³ /at)
AlB ₂	−5.736	8.60	−5.623	9.15
TiB ₂	−8.102	8.58	−7.712	9.38
VB ₂	−8.161	7.87	−8.067	8.39
WB ₂	−8.777	8.94	−9.037	9.30

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