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Solid solution hardening of vacancy stabilized $Ti_xW_{1-x}B_2$

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ABSTRACT

We present a combined experimental and theoretical investigation of sputter deposited thin films in the ternary system $Ti_{1-x}W_xB_2$. Solid solutions of $Ti_{1-x}W_xB_{2-z}$ were prepared by physical vapor deposition (PVD) and, over the whole composition range, found to crystallize in the AlB_2 structure type. The obtained films exhibit good thermal stability and high hardness, evidencing a maximum value of almost 40 GPa for $Ti_{0.67}W_{0.33}B_{2-z}$. The effect of vacancies on stabilization and mechanical properties of the AlB_2 structure type is discussed, using ab initio simulations. Based on our results, we can conclude that vacancies are crucial for the phase stability of PVD deposited $Ti_{1-x}W_xB_{2-z}$ coatings.

1. Introduction

The increasing industrial demand for protective coatings with high hardness, good elastic properties and thermal stability calls for the investigation of new material systems. Although transition metal (TM) nitrides are successfully applied for different tasks in automotive or aerospace industries, the search for improved materials is an ongoing topic, being far from its end.

It is well known that vapor phase deposition techniques allow the growth of supersaturated solid solutions such as cubic B1 $Ti_{1-x}Al_xN$ (rocksalt structure, NaCl prototype). In case of $Ti_{1-x}Al_xN$, the supersaturation of the TiN-based cubic structure increases with higher Al fractions. At elevated temperatures, this allows for self-hardening effects, resulting from spinodal decomposition and formation of TiN- and AlN-rich cubic domains [1–3]. Only the transition from cubic to wurtzite AlN, which takes place upon further annealing, typically results in a loss of mechanical properties, may, however, due to the enormous volume change, induce a toughening effect for controlled AlN phase fractions [4]. Thus, the unique properties of $Ti_{1-x}Al_xN$ originate from the interplay and competition of two phases, preferring different structure types – cubic TiN and wurtzite AlN.

Making use of the concepts on which the exceptional properties of $Ti_{1-x}Al_xN$ are based, ternary borides have recently been suggested as promising candidates for strong materials with exceptional properties [5]. However, while ternary and even quaternary TM nitrides have been investigated in detail, multinary borides are largely unexplored.

A large number of diborides, including the well-studied and technologically important TiB_2 phase [6–9], prefer the so-called AlB_2 structure type [10] and crystallize in a three atoms unit cell with space group 191 ($P6/mmm$). An instructive description of this structure, as a stacking of hexagonal planes with covalently bonded boron atoms that are separated by metal layers, is given in Fig. 1(a). The boron atoms form graphite-like, covalently bonded hexagons, with metal atoms above (and below) their centers. In addition to the predominant AlB_2 structure type, different structural modifications of diboride phases are known. One such example is WB_2, for which two different modifications are reported [11–14]. Recently, WB_2 thin films were reported to crystallize in the AlB_2 structure, whereas bulk material prefers the WB_2 modification, formerly known as W_2B_5. The WB_2 structure type is closely related to the AlB_2 prototype but evidences a different layer structure, with both flat and puckered boron layers. This results in an increased unit cell, containing twelve atoms and crystallizing in space group 194 ($P63/mmc$) as depicted in Fig. 1(b). For simplification, in the following, the AlB_2 structure will be named α-phase, whereas the WB_2 structure type will be refereed to as ω-phase.

In this work magnetron sputtering has been used to deposit $Ti_{1-x}W_xB_{2-z}$ thin films with varying Ti/W ratio. Interestingly, over the whole composition range, the coatings were found to crystallize in the AlB_2 structure type. The films show high hardness, with a maximum value of almost 40 GPa in case of $Ti_{0.67}W_{0.33}B_{2-z}$. Moreover, good thermal stability was evidenced with the films remaining stable after annealing for 30 min at 1000 °C. Finally,

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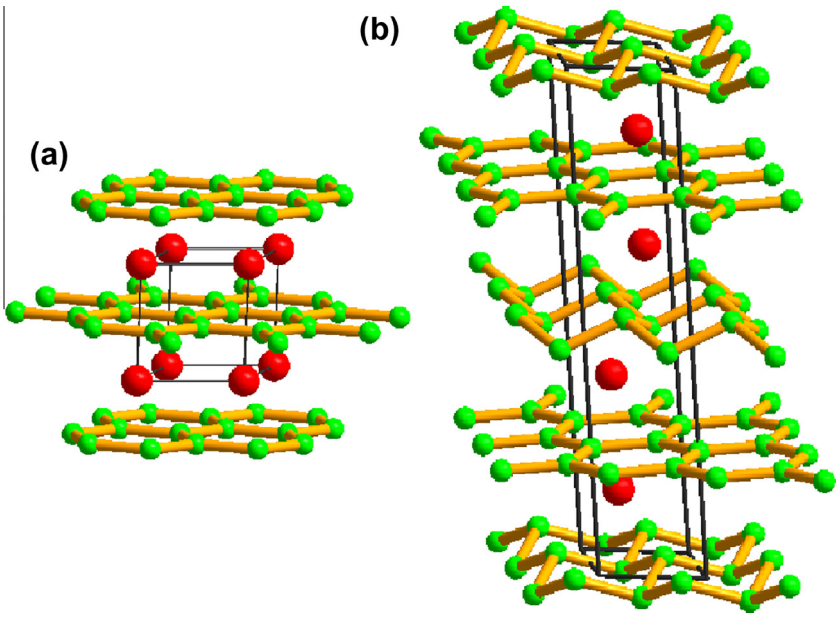

Fig. 1. Unit cell and layer structure of (a) AlB_2 and (b) WB_2 prototypes.

ab initio methods are used to explain the stabilization of α-$Ti_{1-x}W_xB_{2-z}$, evidencing the importance of point defects for PVD deposited materials. Indeed, in case of $Ti_{1-x}W_xB_2$ vacancies are crucial for the phase stability, which is fundamentally different to recent results on $Ti_xAl_{1-x}N$ [15]. This study classifies $Ti_{1-x}W_xB_2$ as a highly interesting material system and moreover underlines the huge impact vacancies may exert on the phase stability of PVD deposited coatings.

2. Experimental and computational methods

Ternary $Ti_{1-x}W_xB_{2-z}$ films have been deposited using an AJA Orion 5 lab-scale magnetron sputtering system. A 3-inch TiB_2 and a 2-inch WB_2 target (Plansee Composite Materials GmbH) were operated by an ENI RPG-100 and an ENI RPG-50 DC pulsed plasma generator with current controlled signal (pulse frequency of 150 kHz, pulse width of 2576 ns). After reaching a vacuum below 10^{-6} mbar, the single crystalline Si ((100) oriented) and polycrystalline Al_2O_3 substrates were heated to a temperature of 700 °C and then ion etched in Ar atmosphere (5×10^{-2} mbar). During deposition, the substrates, at floating potential, were kept at the constant temperature of 700 °C, while a working gas pressure (Ar) of 10^{-2} mbar was used. A deposition time in the order of ~180 min was chosen, resulting in thin films of about 2 µm thickness.

After dissolution with mineral acids, the chemical composition of the as-deposited thin films were determined by inductively coupled plasma atomic emission spectroscopy, also allowing for the determination of the boron content.

The structure of the thin films, deposited on Si and Al_2O_3 substrates, in the as-deposited state and after vacuum annealing at 1000 °C, was investigated by X-ray diffraction, using an Empyrean Panalytical diffractometer in grazing incidence geometry with an angle of incidence of $\omega = 2°$ (CuK_α, wave length $\lambda = 1.54$ Å). Moreover, scanning electron microscopy (SEM) was used to investigate the microstructure of the as-deposited coatings on the Si substrates.

Mechanical properties of the as-deposited coatings on Si substrates were obtained by using an ultra micro indentation system (UMIS), equipped with a Berkovich indenter. In order to minimize the substrate interference, loads within a range from 2 to 25 mN were applied. By analyzing the resulting load–displacement curves of the nanoindents after Oliver and Pharr [16], hardness and indentation modulus were determined.

To investigate the respective stability of vacancy-containing $Ti_{1-x}W_xB_2$ structures in α- and ω-modification, density functional theory (DFT) calculations have been conducted. The impact of vacancies on the phase stability of both structural modifications as well as the mechanical properties of the experimentally evidenced α-phase were investigated, using the Vienna Ab Initio Simulation Package (VASP) [17–19], applying the projector augmented waves method and the generalized gradient approximation (PAW–GGA).

In a first step, supercells of both structural modifications of $Ti_xW_{1-x}B_2$ were constructed. In case of α-$Ti_xW_{1-x}B_2$ a $2 \times 2 \times 4$ supercell with 48 atoms was investigated, while for ω-$Ti_xW_{1-x}B_2$ a $2 \times 2 \times 1$ supercell, also containing 48 atoms, was selected. Different chemical compositions were then realized by populating the metal sublattices with the corresponding Ti/W ratios, applying the special quasirandom structure (SQS) approach [20,21]. The SQS structures, obtained by making use of the atat package [21], were optimized with respect to lattice parameter and atom positions by applying the VASP code, using an energy cutoff of 600 eV and a $8 \times 8 \times 4$ Γ-centered k-point mesh. Both energy cutoff and k-point mesh were carefully chosen to ensure energy convergence within a few meV/at. Vacancy containing structures were then investigated by two different approaches. Starting from the defect-free supercells, vacancies were created by randomly removing either a boron or a metal (tungsten) atom, reducing the number of atoms per supercell to 47. In an additional approach, new 47 atoms SQS structures were created, by treating vacancies as further alloying elements. This second approach was applied to exclude effects, resulting from special local environments. For both scenarios, the resulting structures were again optimized, using the same settings as in case of the vacancy-free cells. To further investigate this behavior, an additional vacancy concentration was investigated by introducing two vacancies, a boron and a metal vacancy, into the supercells. Here again the second approach was applied, i.e. new SQS structures were created with vacancies treated as additional alloying elements. For this scenario such an approach is necessary, to avoid coincidental clustering of vacancies. The