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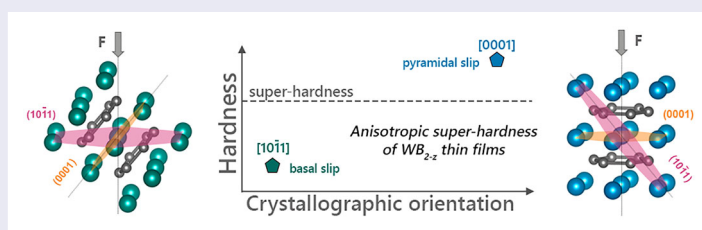
Anisotropic super-hardness of hexagonal $WB_{2\pm z}$ thin films

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ABSTRACT

Transition metal diboride-based thin films are promising candidates to replace state-of-the-art protective and functional coating materials due to their unique properties. Here, we focus on hexagonal WB_{2-z} , showing that the AlB_2 structure is stabilized by B vacancies exhibiting its energetic minima at sub-stoichiometric $WB_{1.5}$. Nanoindentation reveals super-hardness of 0001 oriented α - WB_{2-z} coatings, linearly decreasing by more than 15 GPa with predominant $10\bar{1}1$ orientation. This anisotropy is attributed to differences in the generalized stacking fault energy of basal and pyramidal slip systems, highlighting the feasibility of tuning mechanical properties by crystallographic orientation relations.



IMPACT STATEMENT

First report of an anisotropic elastoplastic behaviour in super-hard PVD AlB_2 structured WB_{2-z} . Theoretical and experimental verification of thermodynamically most stable sub-stoichiometric α - WB_{2-z} coatings by structural and mechanical analysis.

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KEYWORDS

WB_2 ; physical vapour deposition; DFT; structural defects; anisotropy; super-hardness

Introduction

Transition metal diborides (TMB_2) exhibit a tremendous potential to be applied in various applications ranging from wear- and corrosion resistant coatings, superconductive thin films, up to extremely stable protective layers [1–4]. Diborides of group 2–5 prefer to crystallize in the hexagonal AlB_2 structure (α , space group 191—P6/mmm), while TMB_2 of group 6 and higher typically reveal the so-called W_2B_5 based structure (ω , space group 194—P6₃/mmc) [5,6]—except for CrB_2 [7,8]. Frottscher et al. already pointed out, that the pretended Mo_2B_5 and W_2B_5 are Mo_2B_4 and W_2B_4 , whereas only non-stoichiometric compounds $TMB_{2\pm z}$ prefer to crystallize in the α -structure [9]. Nevertheless, due to strongly limited kinetics during physical vapour deposition (PVD), WB_{2-z} is stabilized in its metastable α -phase rather than in the thermodynamically preferred

ω structure [10–12]. Structural defects—being predominant in PVD materials—are presumed to stabilize the α -phase. This is confirmed in detail for the TiB_2 material system, where sub-stoichiometric $TiB_{1.9}$ is stabilized by the absence of B between Ti-planes locally relaxing the structure [13].

In general, the enhanced hardness of hexagonal material systems is related to limited slip systems (slip plane and -direction)—compared to cubic systems—impeding dislocation movement and thus, plastic deformation [14]. Furthermore, in hexagonal SiC and GaN the dislocation motion and activated slip systems have been described and anisotropic mechanical properties were shown [15–19]. The experimental observations of SiC single crystal polytypes revealed higher hardness of basal indentations compared to prismatic indentations [15]. Moreover, Huang et al. indicated specific slip planes being

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active during plastic deformation of GaN, suggesting that anisotropic elastoplastic mechanical properties correlate with plastic deformation [17]. In contrast, no distinct orientation-dependent fracture toughness could be detected so far [15,18].

Moreover, $\text{WB}_{2\pm z}$ is known for its enhanced material properties like hardness, Young's modulus as well as fracture toughness, and therefore often consulted as a base system forming ternary $\text{TM}_I\text{TM}_{II}\text{B}_{2\pm z}$ [10,11,20,21]. In previous studies, we successfully showed the positive effect of Ta alloying on the mechanical properties (H, K_{IC}), thermal stability, and oxidation resistance of $\text{WB}_{2\pm z}$ thin films [10,21,22].

The focus of this study is to obtain new insights into the elastoplastic behaviour of $\text{WB}_{2\pm z}$ thin films concerning their detailed structural constitution using different structural as well as micro-mechanical characterization techniques. Furthermore, theoretical investigations using ab initio methods should clarify structural uncertainties of the AlB₂ type $\text{WB}_{2\pm z}$.

Experimental

Computational details

DFT coded VASP [23,24] calculations using the projector augmented waves method within the generalized gradient approximation (PAW-PBE) [25] were applied to investigate the energy of formation (E_f) and elastic constants of α - and ω -structured WB_x cells ($x = 2\pm z$). The perfect, as well as the defected structures, were generated using the SQS special quasirandom structure (SQS) approach. The elastic constants were calculated using the stress/strain method [26], further details are described in the Supplementary Material.

Thin film synthesis

To offer a broad spectrum of deposition parameters beyond temperature, pressure, and bias, we used three different deposition systems. An in-house developed magnetron sputtering system (for details see Supplementary) an AJA International Orion 5 magnetron sputtering system, and an Oerlikon Balzers Innova deposition system providing diverse sputter configurations with different target-substrate distances and angles. The coating facilities have been equipped with six-inch and three-inch powder-metallurgically prepared W_2B_4 targets—manufactured by Plansee Composite Materials GmbH—exhibiting the ω -structure. The deposition processes were carried out in pure argon with a rotating substrate holder. For detailed information to the in-house developed system and on the varied parameter

settings on each deposition system, see Table S1–3 in the Supplementary.

Characterization methods

For detailed structural characterization of all coatings deposited, a Philips XPERT diffractometer in Bragg–Brentano configuration, as well as the nanofocus endstation (DESY Petra III), were used (selected samples).

Hardness (H), and Young's modulus (E), of all films, were investigated by an Ultra Micro-Indentation System (UMIS), equipped with a Berkovich diamond tip. The resulted loading and unloading curves were evaluated after Oliver and Pharr [27] to gain H and E, respectively.

The elemental composition of selected films on Si substrates was analyzed by liquid inductively coupled plasma optical emission spectroscopy (ICP-OES). LICP-OES measurements were carried out on an iCAP 6500 RAD (Thermo Fisher Scientific, USA), with an ASX-520 autosampler (CETAC Technologies, USA) using an HF resistant sample introduction kit, consisting of a Miramist nebulizer (Burger Research, USA), a PTFE spray chamber and a ceramic injector tube. The WB_{2-z} coatings were acid digested with the method presented and validated in [28–30]—described in detail in the Supplementary Material.

In addition, one selected sample was surveyed by transmission electron microscopy (TEM FEI TECNAI, F20, acceleration voltage of 200 kV). Detailed structural information was gained by selected area electron diffraction (SAED). The sample preparation was done by focused ion beam (FIB, Quanta 200 3D DualBeam), applying a standard lift-out technique [31].

In situ micromechanical bending tests of substrate-free coating cantilevers are conducted to obtain the fracture toughness of selected coatings. The experiments were performed within an SEM equipped with a Hysitron PI-85 SEM pico-indenter whose spherical diamond tip was pressed onto the top of the pre-notched cantilever (in the growth direction of the coatings) until fracture [32]. The calculation of the fracture toughness was performed after Matoy et al. [33]—see also Supplementary Material.

Results and discussion

DFT calculations revealed the energy of formation, E_f , of perfect and defected α - and ω -structured $\text{WB}_{2\pm z}$ cells. In Figure 1(a) the development of E_f with increasing B vacancies (blue filled squares for α , red filled triangles for ω), W vacancies (blue half-filled squares for α , red half-filled triangles for ω) and Schottky defects (blue empty

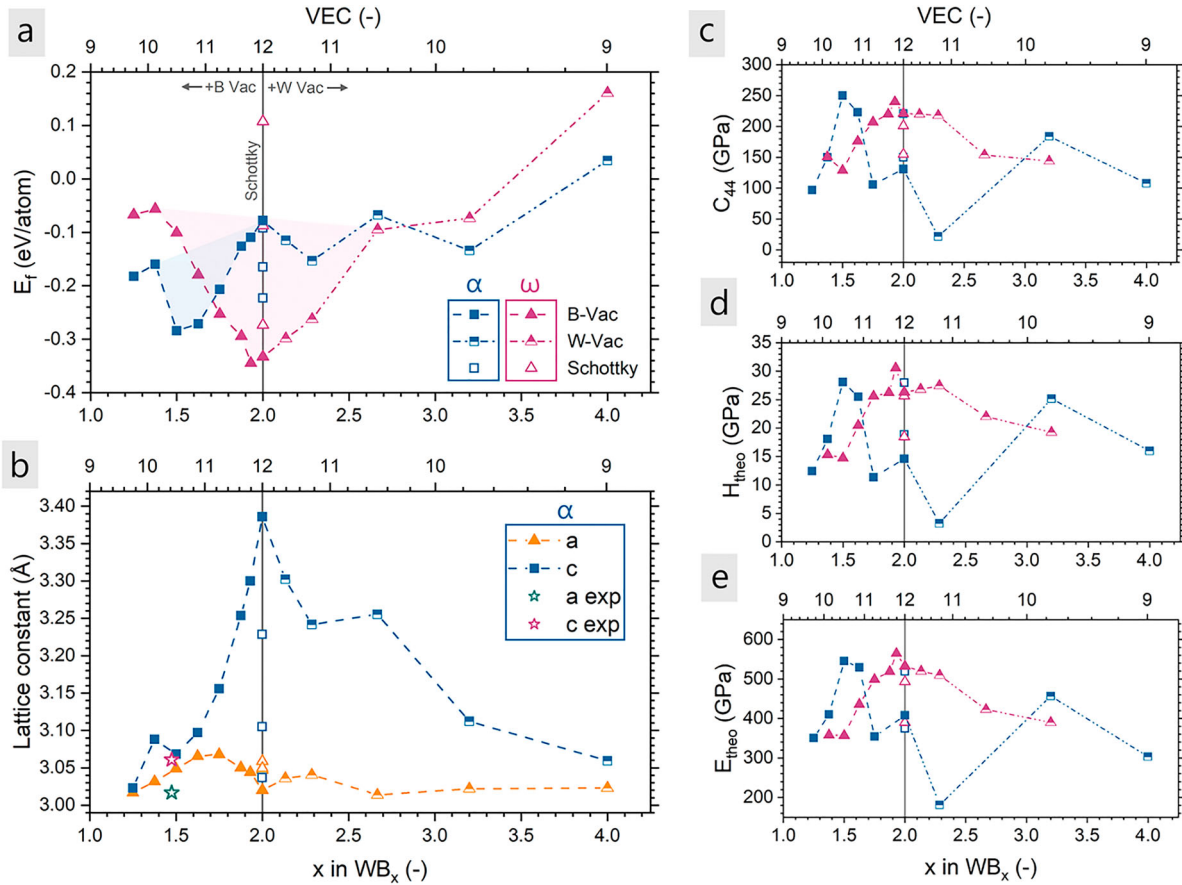


Figure 1. (a) E_f values of fully converged α -WB $_x$ ($2 \times 2 \times 4$) and ω -WB $_x$ ($2 \times 2 \times 1$) supercells ($x = 1.25$ – 4.0) as a function of chemical composition represented by the value of $x = 2 \pm z$ in WB $_x$. Figure 1b gives the evolution of lattice constant a (orange triangles), and c (blue squares) of α -WB $_x$. Additionally, the elastic constant C_{44} (c), the theoretical hardness H_{theo} (d), and the theoretical Young's modulus E_{theo} (e) of all mechanically stable structures are illustrated. The change in valence electron concentration (VEC) of defected WB $_x$ crystals is depicted in the abscissa on top of Figure 1a–e.

squares for α , red empty triangles for ω), is indicated, respectively. The vertical grey line represents stoichiometric WB $_2$ expressing the value of $x = 2.0$ in WB $_x$. With increasing B vacancy population x is decreasing, while an increase of W vacancies leads to an increase of x (indicated on the bottom abscissa of Figure 1(a)). Moreover, an increasing vacancy concentration is decreasing the valence electron concentration (VEC) of the material system, highlighted on the top abscissa of Figure 1(a).

Generally, E_f raises by adding vacancies to the ω -lattice, having its minima around the perfect W $_2$ B $_4$ /WB $_2$ stoichiometry [9] and lowered with increasing number of vacancies within the α -lattice. The α -structured cell is thermodynamically preferred compared to ω —meaning E_f of α -WB $_{2-z}$ is below ω -WB $_{2-z}$ —at a vacancy concentration $> 6\%$. Boron defected α - and ω -structured cells energetically intersect at WB $_{1.70}$ ($E_f = -0.23$ eV/at) followed by a thermodynamic minimum at WB $_{1.50}$ ($E_f = -0.28$ eV/at) for the α -lattice. The atomic concentration of the α -cell at the E_f minima leads to 40 at.%

W and 60 at.% B, hence matching the experimentally measured compositions obtained by ICP-OES for various WB $_{2-z}$ films deposited on the different routes (WB $_{2.01}$: W = 40.74 ± 0.91 at.%, B = 59.26 ± 0.91 at.%; WB $_{2.20}$: W = 39.14 ± 1.67 at.%, B = 60.86 ± 1.67 at.%; WB $_{2.21}$: W = 40.41 ± 2.04 at.%, B = 59.59 ± 2.04 at.%). Moreover, investigations on the evolution of α -WB $_{2 \pm z}$ lattice constants revealed convergence of α -WB $_{1.5}$ ($a = 3.0488$ Å, $b = 3.0483$ Å, $c = 3.0683$ Å, $V = 24.74$ Å ^{3}) during DFT calculations with our experimentally obtained values of WB $_{1.47}$ ($a = 3.0168$ Å, $c = 3.0608$ Å) using nanobeam diffraction on powdered coating material (stars in Figure 1(b))—for details see Supplementary. Due to correlating lattice parameters from our α -WB $_{1.47}$ with those reported from Woods et al. ($a = b = 3.0200$ Å, $c = 3.0500$ Å, $V = 24.09$ Å ^{3}) [34], we would suggest a sub-stoichiometric composition also for their structure. In addition, Hayami et al. theoretically determined lattice constants for WB $_{1.625}$ of $a = b = 3.072$ Å, $c = 3.117$ Å [35].

All defected lattice configurations (considered in Figure 1(a)) have been consulted for calculating the stiffness tensor C . To ensure validity of the resulted elastic constants C_{ij} , the following criteria have to be fulfilled in hexagonal crystals: $C_{11} > |C_{12}|$; $2C_{13}^2 < C_{33} \cdot (C_{11} + C_{12})$; $C_{44} > 0$; $C_{66} > 0$. All data points presented in Figure 1(b–d) satisfy the above-mentioned stability conditions, thus revealing mechanically stable structures. For the quantification of mechanical stability of perfect and defected structures, the elastic constant C_{44} is highlighted in Figure 1(c). The data points reveal values of $C_{44} = 131$ GPa for stoichiometric α as well as $C_{44} = 221$ GPa for ω , indicating enhanced mechanical stability for ω . This trend is inverted by introducing B vacancies to the crystal structures leading to a maximum $C_{44} = 250$ GPa at $x = 1.5$ and $VEC = 10.5$ for α structured $WB_{1.5}$. Moreover, the C_{44} maximum of the α -lattice is correlating with the E_f minima (Figure 1(a)), revealing highest thermodynamic stability is also leading to the highest mechanical stability of this crystal. Furthermore, theoretical hardness values, H_{theo} , have been evaluated using a widely established model [36], $H = 0.92 \cdot (G/B)^{1.137} \cdot G^{0.708}$, where G and B are shear and bulk modulus, respectively. Figure 1(d) illustrates H_{theo} , showing a maximum value of $H_{theo} = 28$ GPa for α structured $WB_{1.5}$ and maximum $H_{theo} = 31$ GPa for ω - $WB_{1.93}$. The same trend was experienced for the theoretical Young's moduli ($E = 9 \cdot B \cdot G / (3B + G)$) with a maximum $E_{theo} = 546$ GPa for α structured $WB_{1.5}$ and $E_{theo} = 565$ GPa for ω - $WB_{1.93}$, as indicated in Figure 1(e).

Although the used target material is of ω - WB_2 structure, the deposition of ω - WB_2 coatings points out to be very challenging, since α -structured WB_{2-z} is preferentially formed within magnetron sputtering techniques (see XRD patterns in the Supplementary Material). The broad parameter variation on 3 different deposition systems revealed always sub-stoichiometric α - WB_{2-z} structured thin films but in various crystal orientations. The reason for the alpha stabilization is the high defect density especially on the non-metal sublattice (dislocations, vacancies) due to the extreme cooling rates during condensation from the vapour phase to the solid state. Furthermore, the difference in mass between light (B) and heavy (W) elements promotes scattering effects during sputtering leading to sub-stoichiometric compositions. A highly 0001 oriented α - WB_{2-z} coating ($WB_{1.45}$) has been investigated using TEM (see Figure 2). The coating exhibits a columnar and defected morphology, see Figure 2(a,b). Section 2a also represents the area for the recorded SAED pattern, depicted in the inset a-i. SAED exhibits highly oriented crystals in $[11\bar{2}0]$ zone axis. Additionally, the inset a-i contains a VESTA

model [37] of the α -structured WB_2 unit cell—the W and B atoms are represented in red and blue, respectively—oriented as obtained from SAED. Figure 2(b) shows a high-resolution TEM image of the investigated coating, emphasizing defected zones within the highly-oriented crystal. However, the FFT image, depicted in section c, confirms the same crystal orientation as already revealed from SAED—masking regions for the Inverse Fast Fourier Transform (IFFT) are marked as white dashed circles. The sections d-f show filtered TEM images (for technical details see [38]) from the same region marked in b overlaid with a masked IFFT in the depicted directions ((1000) , (0001) , and $(10\bar{1}1)$ for d, e, and f respectively). Conducting this procedure, defect/strain-rich domains can be highlighted, confirming the structural stabilization in the α -phase of the chemically sub-stoichiometric $WB_{1.45}$ film. In correspondence to [13], structural defects (i.e. Boron vacancies) seem to compensate for the sub-stoichiometry of the coating.

In Figure 3(a) experimentally determined hardness H (blue open squares) and Young's modulus E (red open triangles) are plotted as a function of increasing fraction of 0001 lattice orientation of the various α - WB_{2-z} coatings. H is increasing from ~ 25 GPa for coatings without any 0001 orientation up to ~ 40 GPa for purely 0001 oriented coatings. Thus, the dataset reveals a linear dependency of H with an increasing 0001 ratio (see linear fit with 95% confidence limit in Figure 3(a)). On the other hand, the evaluation of the $10\bar{1}1$ ratio shows a contrary picture. Figure 3(b) depicts the experimentally determined H as a function of increasing $10\bar{1}1$ ratio (blue open squares), revealing a decrease of H with an increasing $10\bar{1}1$ orientation (blue dashed line and blue shaded area). These results point out the anisotropic mechanical property of α - WB_{2-z} coatings, revealing the highest hardness when 0001 oriented by simultaneously showing no $10\bar{1}1$ orientation. In comparison, the stoichiometric α -structured WB_2 is predicted to obtain a $H_{theo} = 15$ GPa, whereas the boron defected α - $WB_{1.5}$ reveals $H_{theo} = 28$ GPa coinciding with the experimental data. Here, we need to point out that in H_{theo} neither anisotropic effects nor hardening due to a Hall-Petch effect is considered.

The observed anisotropy in hardness can be related to aggravated dislocation movement due to energetically less preferred slip systems. Through DFT, Hunter et al. [39] showed that various slip systems in hexagonal ZrB_2 (AlB_2 prototype, SG191, α) reveal different generalized stacking fault energies (GSFE). The $\langle a \rangle$ type basal slip 0001 is the easiest a-type slip system to activate, energetically followed by pyramidal $\langle \bar{1}2\bar{1}0 \rangle$ $10\bar{1}\bar{1}$ and both prismatic $\langle 1120 \rangle$ $10\bar{1}0$ slip systems. Additionally, the

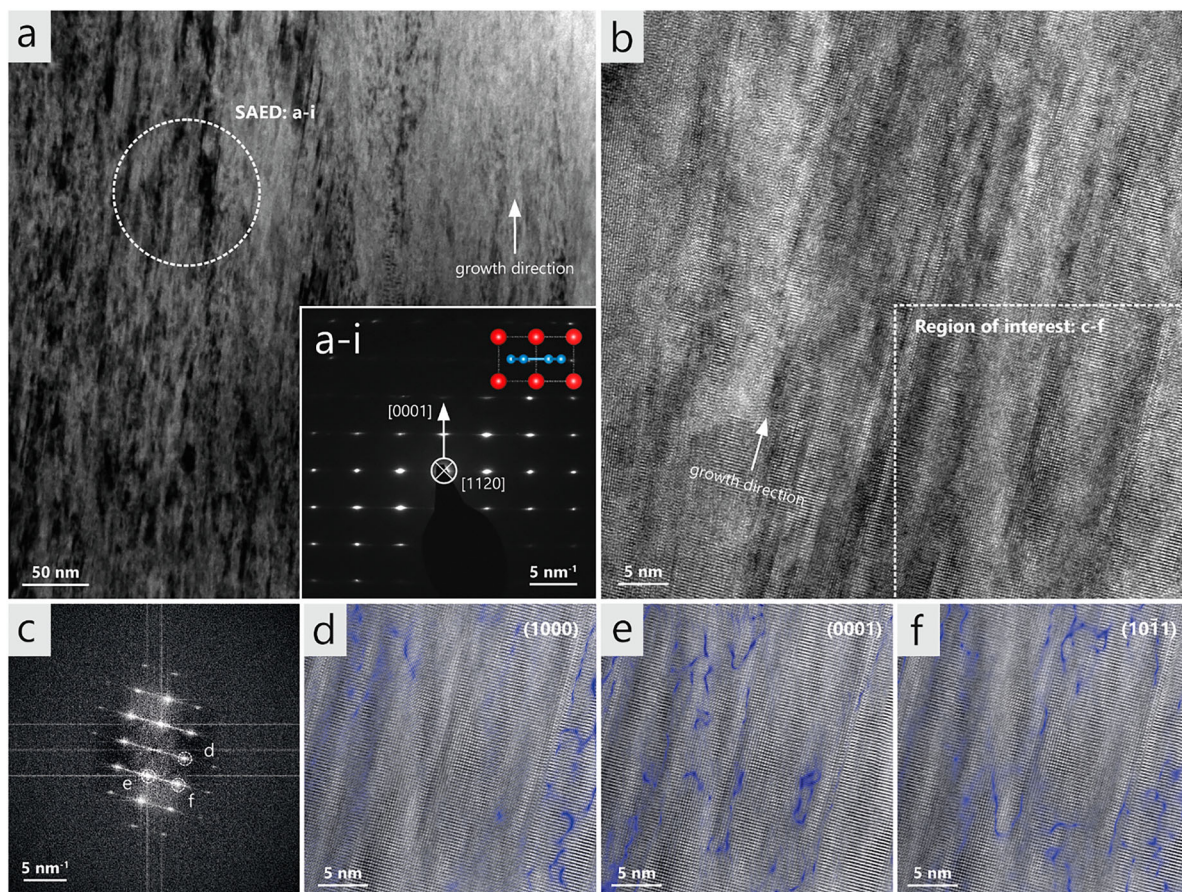


Figure 2. TEM analysis of the WB_{1.45} coating. Section a presents a cross-sectional BF image of the WB_{1.45} lamella, pointing out the area for the recorded SAED (white dashed circle) displayed in the inset a-i. An FFT cut out of the HR-TEM in b (region of interest) is depicted in section c, furthermore marking the masking regions for the IFFT as white dashed circles. Section d-f show defect/strain rich domains corresponding to the indicated directions (based on IFFT).

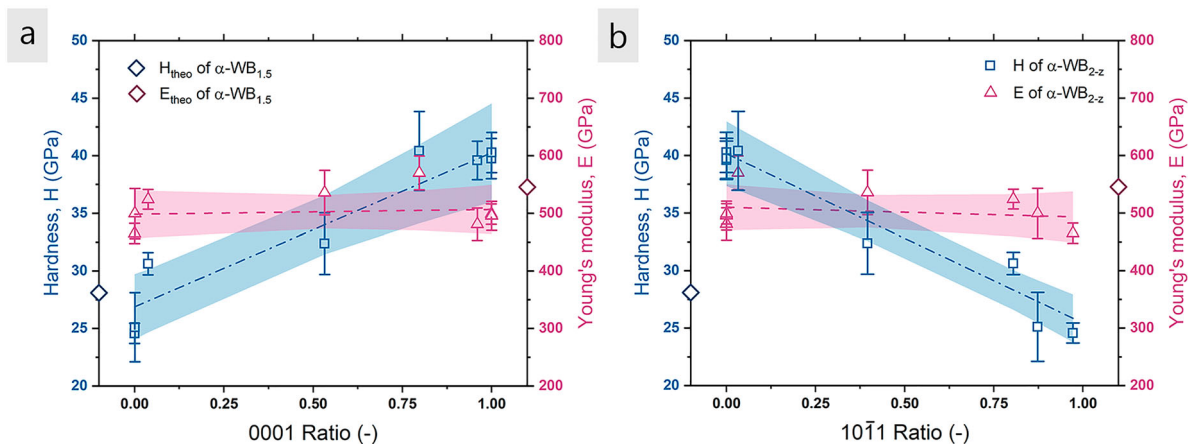


Figure 3. Hardness H (blue open squares) and Young's modulus E (red open triangles) of various α -WB_{2-z} thin films deposited. The dataset presents the mechanical properties as a function of the 0001 (a) and $10\bar{1}1$ lattice plane (b) orientation factor, determined from XRD data (see Supplementary Material). The dashed lines give a linear fit from H (blue dashed line) and E (red dashed line). The blue and red shaded areas represent a 95% confidence limit.

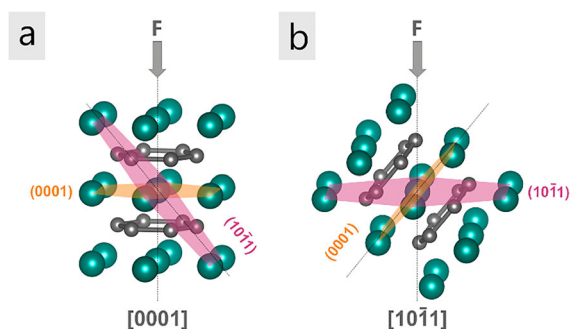


Figure 4. The hexagonal α -WB₂ structure is illustrated in 0001 (a) and 10 $\bar{1}1$ (b) orientation. W and B atoms are depicted in green and grey, respectively. Indentation experiments leading to a normal force F (grey arrow) which is appearing perpendicular to the (0001) plane (a) (basal slip plane, orange area) or (10 $\bar{1}1$) plane (b) (pyramidal slip plane, red area).

calculated GSFE values are correlating with interplanar spacing, meaning the closer the planes are spaced, the larger the GSFE value becomes. Due to structural correlations of α -ZrB₂ and α -WB_{2- z} , we can assume a similar behaviour for both hexagonal material systems. Thus, a hardness increase for [0001] crystals can be explained by a larger GSFE value of the pyramidal slip system (10 $\bar{1}1$ slip plane)—compared to the basal slip system—which experiences the maximum shear stress τ_{max} when a force (during indentation) is applied in [0001] direction (see Figure 4(a)). However, for a 10 $\bar{1}1$ crystal, the basal slip system (0001 slip plane) is preferentially activated due to τ_{max} appearing at a 45° angle to the force vector F (Schmid's law), directing in [10 $\bar{1}1$] in this scenario (see Figure 4(b)).

In contrast to the hardness results, indentation experiments revealed relatively constant Young's moduli in the range of ~ 500 GPa, depicted in Figure 3(a,b). The data set emphasizes that the 0001 and 10 $\bar{1}1$ crystal orientations have only a minor influence on E (depicted by the linear fit; red dashed line). For comparison, the DFT calculations exhibit a Young's modulus of 408 GPa for perfect α -WB₂ structured cells. Only after introducing B vacancies, the theoretical Young's modulus increases to $E_{theo} = 546$ GPa for α -WB_{1.5} approaching the experimentally observed data. Moreover, by evaluating the spatial dependency of the Young's modulus of perfect α -WB₂ and defected α -WB_{1.5} a clear decrease of the anisotropy for the α -WB_{1.5} could be observed (see Figure S4 and S5 in the Appendix). The anisotropy reduces from 1.804 for α -WB₂ to 1.151 for α -WB_{1.5} further underlining the presence of a highly defected structure within our WB_{2- z} thin films.

In addition to the anisotropy of the hardness, we also evaluated the fracture toughness of selected coatings to gain a deeper insight into a possible orientation-related

fracture behaviour. Micromechanical cantilever bending experiments of selected α -WB_{2- z} coatings, revealed K_{IC} values ranging from 2.89 ± 0.26 MPa $\sqrt{m}$ (WB_{1.45}, 0001-ratio: 0.80), 3.23 ± 0.19 MPa $\sqrt{m}$ (WB_{1.87}, 0001-ratio: 0.99), to 3.65 ± 0.26 MPa $\sqrt{m}$ (WB_{1.55}, 0001-ratio: 0.04), revealing no perceptible influence of the film orientation (for further details see Table S4 in the Supplementary Material). The results indicate that the fracture toughness of our thin film materials is not affected by dislocation movement, hence other mechanisms govern the observed variation in K_{IC} values. Such mechanisms can be for example: the cohesive grain boundary strength (influenced by the growth conditions or the introduction of column boundary affine elements), introduction of third order residual stresses by i.e. precipitation toughening or unwanted impurities such as oxygen, or effects of the microstructure on the fracture behaviour.

Conclusion

In summary, the AlB₂ structure formation of WB_{2 $\pm z$} was investigated by DFT. The calculations indicate the stabilization of hexagonal α -WB_{2- z} by B vacancies, compared to a thermodynamic minimum of perfect, stoichiometric ω -WB₂. This theoretical result is experimentally underlined by: matching lattice parameters, mechanical properties, and chemical compositions of physical vapour deposited α -WB_{2- z} thin films. Moreover, nanoindentation of the synthesized coatings revealed anisotropy in the elastoplastic behaviour. Super-hardness was determined for 0001 oriented films, linearly decreasing by more than 15 GPa with an increasing 10 $\bar{1}1$ orientation. Varieties in GSFE of basal and pyramidal slip systems in hexagonal crystals may constitute anisotropy in hardness. In contrast, no impact of the crystal orientation on K_{IC} could be detected.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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