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Strategic lattice manipulation in transition metal nitrides for improved solubility

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ABSTRACT

In this study, we propose a new concept for achieving metastable ternary transition metal nitride solid solutions, focusing on face centered cubic (fcc) structured Ti(N,B) as a model system. Combining non-reactive magnetron sputtering with computational analysis, we develop a microalloying strategy to manipulate the metallic sublattice, thereby influencing the solubility of B in the non-metal sublattice. We show that imposed tensile strain on the fcc-TiN lattice facilitates the solubility of B, with a 1.5 % strain enabling the incorporation of ~28.5 at.% B at the non-metal sublattice. Conversely, compressive strain hinders the formation of the fcc-Ti(N,B) solid solution, highlighting the importance of lattice manipulation in controlling solubility. At the same time, our experimental findings reveal that adding larger atoms, such as Zr, to the metal sublattice enhances the solubility of B in fcc-TiN more effectively (~2 at.% Zr proves to be sufficient to solute 10 at.% B in the fcc-TiN lattice) than smaller atoms, like Cr or similar-sized Ti atoms. The size effect of the alloying atoms on the B solubility is further supported by radial distribution function analysis, showing lower local lattice distortions for Zr compared to Cr.

1. Introduction

The growing demand for materials tailored to the dynamic needs of diverse industries continually pushes the boundaries of modern materials science. In the field of ceramic hard coatings, forming solid solutions contribute to the development of materials with improved mechanical and thermal properties—particularly crucial in industries where wear, corrosion, and further environmental conditions can impact the functionality and reliability of materials and equipment. By carefully selecting and controlling the composition of the solid solution, engineers can design coatings with desired characteristics, such as hardness, thermal stability, and chemical inertness [1–5]. Especially in applications demanding superior durability and performance, transition metal nitride hard coatings have emerged as a vital subset, renowned for their exceptional hardness and wear resistance [6–10]. Mainly, titanium nitride (TiN)—achieved through plasma-assisted PVD techniques [11–14]—stands out as a paradigm material system that evolved immensely from its initial use as a protective layer for cutting tools in the

mid-20th century to one of today's most prominent and widely used (and studied) coating system in industry (and science), driven by its exceptional range of advantageous functionalities [15–17]. Based on its crystal structure TiN can be explained as an interstitial compound. According to Hägg's rule [18,19], the smaller N atoms occupy the octahedral sites (interstitials) between the larger atoms (Ti) in a face centered cubic (fcc) structured arrangement (according to the NaCl prototype; therefore TiN sometimes has the pre-index of rs for rocksalt). The mix of strong covalent Ti–N and metallic Ti–Ti bonding is what gives TiN high hardness and electrical conductivity [20].

The alloy design of fcc-TiN-based coatings, has demonstrated success with well-established ternary systems such as fcc-(Ti,Al)N [21,22] alongside fcc-Ti(N,C) [23], where solid solutions form upon the introduction of additional elements to the titanium nitride matrix. In case of ternary transition metal nitrides system, we have to compare substitution on the metal-sublattice with substitution on the non-metal-sublattice [3]: For fcc-(Ti,Al)N, Al randomly substitutes for Ti on the metal-sublattice [24,25], whereas the non-metallic C atoms

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replace N in the non-metal sublattice [26,27]. In the case of Ti–Si–N [28], the reverse is desirable; ideally, no Si-solubility should occur in this material system to precipitate a Si-rich phase at the grain boundaries and thus lead to Hall-Petch hardening [29–31].

The synthesis of ternary transition metal nitride thin films is an enticing prospect, as it offers the potential of superior properties compared to their thermodynamically stable binary phases [32,33]. The inherently meta-stable nature of many ternary nitride phases, however, complicates their feasibility [34–36]. Although their structural arrangement does not align with the lowest-energy states—akin to points above the convex hull—metastable phases can persist due to kinetic barriers that impede their transition to the thermodynamically stable configuration [37–41]. Modern methods of plasma-assisted Physical Vapor Deposition (PVD) techniques facilitate the formation of metastable phases due to limited kinetics and non-equilibrium conditions during deposition, explained by pioneering research from W.-D. Münz [42–44], A. Anders [45,46], and D. Depla [47–49]. These conditions of PVD contribute to its popularity for transition metal nitride synthesis by enabling controlled stoichiometry and the ability to fine-tune film properties. While PVD techniques offer unique pathways to access metastable phases [39,40], our research focuses on challenges in synthesizing single-phase fcc-Ti(N,B) thin films. Unlike for ternary nitride systems such as fcc-(Ti,Al)N, where vapor deposition techniques allow for substituting even ~80 at.% of Ti with Al on the metal sublattice [24,50], the solubility of B within the fcc structure of Ti(N,B) [51] coatings is rather limited and preferably TiN+TiB₂ or TiN+BN nanocomposites or mixtures thereof with (amorphous) B-rich grain boundary phases form [3,52–56]. We previously revealed that attaining improved solubility of B within fcc-TiN requires a deviation from the TiN–TiB tie line towards Ti-rich compounds, (i.e., the promoted formation of vacancies on the non-metal sublattice). This deviation was accomplished by non-reactive co-sputtering of a Ti target alongside TiN and TiB₂ targets, where 8.9 at.% B could be fully incorporated into the fcc-TiN lattice (for a non-metal-to-metal = 1:1 stoichiometry, this equals that the non-metal sublattice holds 17.8 at.% B) [52]. In contrast, reactive sputtered coatings tend towards compositions along the TiN–BN tie line [57]. The oversupply of less reactive N₂⁺ ions (relative to Ti⁺ and Ti²⁺) along with an excessive presence of N₂ inhibits the formation of the fcc-Ti(N,B) solid solution and instead forms BN-rich boundary phases [58]. We further concluded that accounting for the required space is necessary when fully incorporating B (0.84 Å) [59] into the fcc-TiN lattice due to its larger size, i.e., larger covalent radius, compared to N (0.71 Å) [59].

By substituting the larger B atoms for the smaller N atoms on the octahedral site, being the preferred lattice site as confirmed by DFT calculations [52,53], the lattice dimensions expand with increasing B concentration. Consequently, this lattice expansion leads to an increase in the lattice parameter—indicated by a shift towards smaller 2θ values in the X-ray diffraction (XRD) patterns—referring to fcc-TiN ($a = 4.255$ Å, calculated). Excess B, however, segregates at the grain boundaries, refining the microstructure of the coating. This incomplete B solubility is also reflected in the XRD analysis, where broader peaks and relatively smaller (or absent) peak shifts appear. Additionally, using HRTEM and EELS, we were able to confirm both the solubility of B and the segregation of excess B at the grain boundaries when B is not fully incorporated into the fcc-TiN lattice [52]. Building on our previous research, here we address the confined spatial conditions for B at the non-metallic sublattice that inhibit the formation of the fcc-Ti(N,B) solid solution. Specifically, we aimed at non-reactive deposition of Ti–Me–B–N coatings (Me=Ti, Zr, or Cr) by strategically increasing the metal content (alloying Ti, Zr, or Cr to a Ti–B–N composite target), while keeping the B content at ~10 at%. Supported by ab initio density functional theory calculations, we explain how the manipulation of the metal sublattice by smaller or larger atoms affects the solubility of B in the non-metal sublattice. Unravelling the size-dependent effects of alloyed atoms on the local stress state of the lattice—where fcc-Ti(N,B) serves as a model

system—we provide a new target-driven microalloying concept to facilitate the synthesis of metastable ternary nitrides.

2. Experimental

2.1. Thin film deposition

The 24 different Ti–Me–B–N (Me = Ti, Cr, or Zr) coatings, in addition to one Ti–B–N coating (prepared from the plain TiN+TiB₂+Ti composite target without additional alloying, referred to as TiB_{0.2}N_{0.8}), were deposited on single crystalline sapphire substrates (1 $\bar{1}02$) $10 \times 10 \times 0.53$ mm³ using a modified Leybold Hereaus LH Z400 MS PVD machine equipped with a 3" unbalanced magnetron source holding a TiN+TiB₂+Ti composite target with an elemental composition of 50 at.% Ti, 40 at.% N, and 10 at.% B, sourced from Plansee Composite Materials GmbH. To facilitate a controlled variation in the deposition of coatings towards higher metal concentrations, we placed an increasing number of Ti, Cr, or Zr pieces ($\sim 3 \times 3 \times 3$ mm³) on the target's race-track. Following ultrasonic cleaning in acetone and ethanol for 5 min each, the substrate preparation commenced inside the chamber after reaching the base pressure below $1 \cdot 10^{-4}$ Pa ($1 \cdot 10^{-6}$ mbar). The substrates were thermally cleaned at ~400 °C for 25 min, and afterwards Ar-ion-etched for 15 min at an Ar pressure (60 sccm Ar-flow) of 67 Pa. At the same time, a negative pulsed voltage of 150 V (150 kHz and 2496 ns on time) was applied to the non-rotating substrate holder with a target-to-substrate distance of 38 mm. Subsequently, all coatings were obtained by non-reactive DC magnetron sputtering at 400 °C by continuously operating the 3-inch Ti–B–N target in current-controlled mode at $I_{\text{Ti–B–N}} = 0.5$ A and keeping the Ar pressure at 0.4 Pa (33 sccm Ar-flow). The deposition time was adjusted between 75 and 90 min to prepare coatings with a thickness t of ~3 μm.

2.2. Chemical analysis

We determined the chemical composition of our coatings (individual elemental concentrations are listed in the Supplementary materials in Table S1) by conducting Time-of-Flight Elastic Recoil Detection Analysis (ToF-ERDA) at the 5 MV Pelletron Tandem accelerator at Uppsala University [60], employing ¹²⁷I⁸⁺ projectiles with a primary energy of 36 MeV. The beam incident angle was 67.5° to the surface normal, with recoils reaching the detector at a 45° angle relative to the direction of the incident beam. The raw experimental data were processed using the CONTES software package [61]. Total systematic and statistical uncertainties were estimated to be below 5 % of the deduced value for the major constituents. Additional chemical information was obtained from X-ray fluorescence (XRF) measurements using a PANalytical AxiosMAX-Advanced spectrometer with a rhodium (Rh) X-ray tube operating at 50 kV and 55 mA under vacuum conditions. The instrument was calibrated using the results of the ERDA-analyzed samples.

2.3. Structural analysis

For structural characterization of the thin films, we performed X-ray diffraction using a PANalytical Empyrean (θ - θ diffractometer) with Cu ($K\alpha_{1,2}$) radiation, equipped with a GaliPIX3D detector. X-ray diffraction patterns were collected over a 2θ angle ranging from 5° to 120° with respect to the sample surface. The lattice plane distances, d_{200} , and full width at half maximum, Γ_{200} , of the 200-peak were determined through peak profile fitting in MalvernPanalytical's HighScore plus software [62] using a Pearson 7 function and an asymmetry type of peaks by splitting width and shape. All diffraction patterns were processed by aligning the prominent [024] sapphire substrate peak to its reference position at $2\theta = 52.534^\circ$ (JCPDS no 00-035-0803) [63].

2.4. DFT calculations

Density function theory (DFT) calculations were performed using the Vienna ab initio simulation package (VASP) [64,65], combined with projector augmented plane-wave (PAW) pseudopotentials [66] and the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA) [67]. These calculations were carried out with a plane-wave cutoff energy of 600 eV and employed an automatically generated Γ -centered k-point mesh with a length parameter of 60 Å.

The 4-atom equilibrated structure of fcc-TiN (Fm-3 m, with a lattice constant of 4.255 Å) served as basis for a 64-atom ($2 \times 2 \times 2$) model for fcc-TiN_{1-x}B_x as well as fcc-Ti_{1-y}Me_yN_{1-x}B_x solid solutions, where B replaces N on the non-metal sublattice and Me={Cr,Zr} replaces Ti on the metal sublattice. The distribution of B atoms followed the special quasirandom structure (SQS) approach [68].

The structures underwent a full optimization (volume, shape, and ionic positions) until forces on atoms were reduced to below 10^{-4} eV/Å, and the total energies of two consecutive ionic steps exhibited a difference of $<10^{-5}$ eV per supercell. For volumetric tension/compression simulations, the supercells were kept at a fixed volume and only the atoms inside were allowed to relax.

Formation energy, E_f , was evaluated consistently with our previous work [52].

The radial distribution functions (RDFs) were calculated using the OVITO package [69]. Subsequently, the misfit strain, ϵ , was evaluated by fitting a Gaussian function to obtain the average bond distance of two individual bonds, the first nearest neighbor distance of the solvent (fcc-TiN lattice) and solute (B), Ti-N and Ti-B, for each material system, and calculated by $\epsilon = (d_{\text{Ti-B}} - d_{\text{Ti-N}}) / d_{\text{Ti-N}}$ [70].

3. Results

To visualize the thermodynamic landscape, we have constructed a quasi-binary convex hull phase diagram (illustrated in Fig. 1), highlighting the metastable nature of the fcc-Ti(N,B) solid solution. Our ab initio Density Functional Theory (DFT) calculations, reveal that the fcc-TiN_{1-x}B_x solid solution is energetically unfavorable compared to the stoichiometrically balanced combination of fcc-TiN, hexagonal close packed (hcp) TiB₂, and hcp-Ti (representing the thermodynamically stable state). Notably, the decomposition reaction into fcc-TiN and fcc-

TiB is even less energetically favorable than the formation of the ternary solid solution, considering that fcc-TiB itself is a metastable compound [71]. In Fig. 1, we highlight the impact of B content on the synthesis of fcc-Ti(N,B) by directly correlating the increasing B-to-N ratio with the rising energy barrier (ΔE_f) that needs to be overcome to achieve the ternary solid solution. The energy gap between the fcc-TiN_{1-x}B_x and its decomposition components (illustrated in blue) widens steadily with increasing B content, approaching the maximum for $x = 1$ ($E_{\text{fcc-TiB}} - E_{\text{fcc-TiN}} = 0.67$ eV/at.). For 10 at.% B (equivalent to 20 at.% on the non-metal sublattice), the fitted data yield a difference of 0.10 eV/at. Although PVD inherently provides a kinetic handle to overcome small ΔE_f , 0.10 eV/at. is rather large for standard PVD processes but not impossible. Considering the E_f barrier of ~ 0.18 eV/at. between the rock-salt (B1) and wurtzite (B4) AlN allotropes [72] we know that B1 AlN can form e.g. via the template effect from fcc-TiN in a superlattice [73].

Although advances in computational materials science enable to predict the stability of solid solutions [5,35,36,74,75], empirical solubility rules stated by Pauling [76–78], Hume-Rothery [79–81], and Hägg [18,19] further allow reasonably estimating the solubility of crystalline materials. Based on Hägg's rule—which predicts the stability of the closest packing for interstitial compounds (Hägg phases)—the ratio of atomic radii of the non-metallic and transition-metallic components (r_x/r_{Me}) must be within the range of 0.41–0.59. The closest packed TiB ($r_x/r_{\text{Me}} = 0.67$) clearly exceeds the limit of 0.59. To meet the limit values of the rule, we used the atomic radii published by Hägg in 1931 [19]. Consequently, it is clear that incorporating B into the fcc-TiN lattice requires a larger metal atom radius, i.e., a larger fcc lattice, further illustrated by comparing the lattice parameters between fcc-TiN ($a = 4.255$ Å) and fcc-TiB ($a = 4.534$ Å), both calculated by DFT.

Having outlined the challenges of synthesizing fcc-Ti(N,B) thin films, we further employ ab initio DFT calculations to address the spatial constraints.

Fig. 2 compares formation energies, E_f , and stresses, $\sigma_{[100]}$, of fcc-Ti(N,B) solid solutions under volumetric tension/compression to those of the fully relaxed system. Specifically, the lattice parameter, a , is fixed to a 1.5 % or 3 % larger respectively smaller value with respect to that of the equilibrium fcc-TiN (i.e., $a = \{4.319; 4.383\}$ Å and $a = \{4.191; 4.127\}$ Å model the system under tensile and compressive strain, respectively, where the reference fcc-TiN exhibits $a = 4.255$ Å. Though having a fixed volume, all strained fcc-Ti(N,B) solid solutions are relaxed in terms of ionic positions (for details see the Methodology). Starting from fcc-TiN, all its strained variants are energetically more costly, as indicated by positive formation energy differences, ΔE_f , from the fully relaxed fcc-TiN. For either tensile or compressive strain, the larger the deviation from the equilibrium lattice parameter, the higher the energetic costs (see the ΔE_f of the 3 % strained TiN being above that of the 1.5 % strained TiN), as we are further away from the thermodynamic equilibrium. Adding B to the N sublattice, ΔE_f gradually increases for all fcc-Ti(N,B) solid solutions under compression. This is because the lattice parameter of fcc-Ti(N,B)—with no strain applied—increases with rising B content, i.e., increasingly deviates from that of the compressed system (see Fig. 2b). Contrarily, the lattice parameter of fcc-Ti(N,B) under tension steadily approaches that of the fully relaxed system—mirrored by decreasing ΔE_f —until reaching the equilibrium value. In case of 1.5 % tensile strain, the overlap occurs at ~ 28.5 at.% of B where $\Delta E_f \sim 0$ eV/at. (the corresponding lattice parameter is marked in Fig. 2b). Note that in order to match the lattice parameter of fcc-TiB ($a = 4.534$ Å), the lattice parameter of fcc-TiN would have to be 6.6 % larger (corresponding to a 6.6 % volumetric tension).

Trends in the formation energy differences between volumetrically strained and fully relaxed fcc-Ti(N,B) solid solutions (Fig. 2a) are further underpinned by evolution of the corresponding stress states. Specifically, Fig. 2c shows the stress tensor component along the strained direction, [001], which is (nearly) equal to the stress tensor components along [010] and [001] (differences come from the numeric). Although at

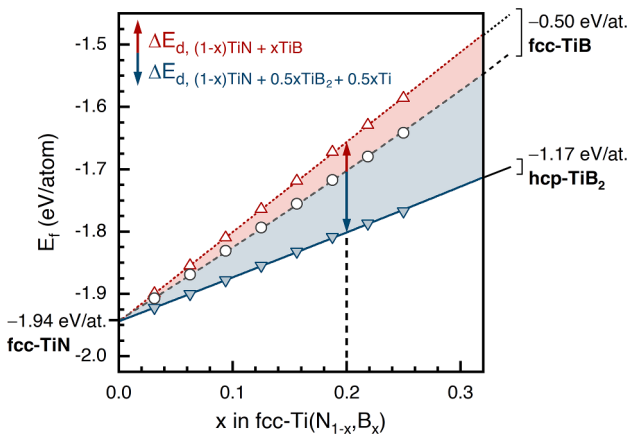


Fig. 1. Thermodynamic stability quantified by the formation energy, E_f , of fcc-TiN_{1-x}B_x compared to its competing decomposition products. The black circular symbols denote E_f for fcc-TiN_{1-x}B_x solid solution along the quasi-binary TiN–TiB tie line. For each composition (shown as a function of x), the location of the energetically more (or less) favorable binary components fcc-TiN+hcp-TiB₂+hcp-Ti (or fcc-TiN+fcc-TiB) is indicated by blue (or red) triangles. The vertical distance between the points, illustrated by a blue and red arrow for $x = 0.2$, equals ΔE_f . Note that the decomposition products are stoichiometrically balanced according to the elemental composition of the educt fcc-TiN_{1-x}B_x.

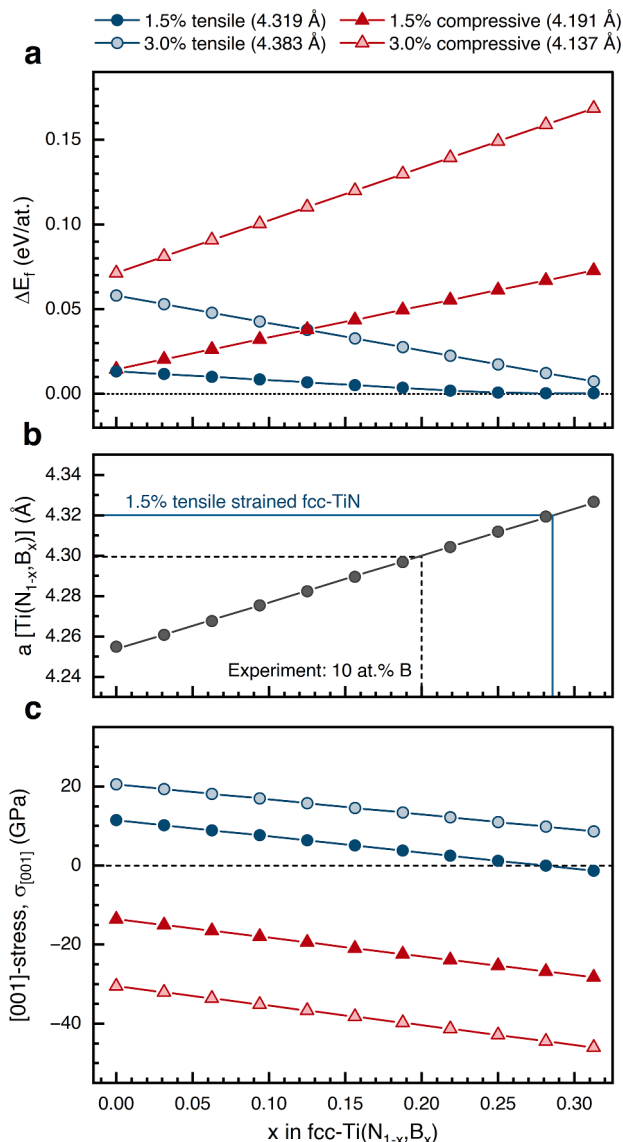


Fig. 2. The impact of volumetric tensile/compressive strain on the energetic stability and stress state of fcc-Ti(N,B) solid solutions as a function of the B content. (a) Formation energy differences, ΔE_f , between volumetrically strained and fully relaxed systems. Taking the parameter of fcc-TiN ($a = 4.255$ Å) as a reference, tensile strain (blue circular data points)/compressive strain (red triangular data points) is applied by enlarging/shortening the lattice parameter (by 1.5 % and 3 %). (b) Lattice parameter of a fully relaxed fcc-Ti(N_{1-x}B_x) plotted against the B content. The B content for which the lattice parameter overlaps with that of the 1.5 % strained system is highlighted by a blue line. The black line denotes the resulting lattice parameter corresponding to the 10 at.% B in our experiment. Likewise, if the solubility of B is reduced purely to its size, a necessary minimum size of the fcc-TiN unit cell modified by microalloying can be determined for certain B alloy contents. (c) Strain-induced stress along the [001] crystallographic direction, i.e., along the applied (tensile/compressive) strain, evaluated for the supercells in (a).

higher B contents, these volumetrically-strained systems exhibit also non-zero shear stresses (0–1.3 GPa), we analyze only (the dominant) tensile or compressive stresses. Concerning volumetric compression, the [001] stresses increasingly deviate from the fully relaxed (thus, stress-free) fcc-Ti(N,B), consistent with increasing ΔE_f in Fig. 2a. Contrarily, stresses on the tensile-strained system diminish with increasing the B content until they nullify. In combination with (approx.) zero E_f difference from the stress-free fcc-Ti(N,B), this mirrors the fact that lattice parameter of the stress-free and tensile-strained system are equal (at this

B content).

To experimentally address the spatial constraints on B in the fcc-TiN lattice, we conducted our study using a composite target of TiN, TiB₂, and Ti with an elemental composition of 50 at.% Ti, 40 % at.% N, and 10 % at.% B. By microalloying additional metals, Me = Ti, Cr, or Zr (achieved by placing metal pieces on the racetrack of the target), we progressively increased the metal concentration. To focus, in particular, on the effects of metallic microalloying, we have deliberately set the B content to 10 at.% in the specified target composition. Fig. 3a-c illustrate the chemical compositions of the deposited coatings (as determined by ToF-ERDA and XRF), displaying a nearly linear progression toward the metal corner within the partial section of the ternary phase diagram. However, the B content of each of the 25 Ti-Me-B-N coatings was maintained at almost 10 at.% (which corresponds to ~20 at.% on the non-metal sub-lattice if B is solely substituting N). The elemental composition of all deposited coatings is listed in the Supplementary Materials in Table S1. Fig. 3d-f illustrate the correlation between the B/N ratio and the three deposited coating series. The data indicates no statistically significant correlation between the two parameters. The decrease in B and N with increasing alloying content is because upon adding Ti, Cr, and Zr metals onto the target-race-track also the B and N source (the target itself) is partly covered. According to our previous DFT calculations [52], B substitutes for N on the non-metal sublattice, while Ti, Cr, and Zr atoms occupy the metal side. Microalloying shifts the chemical composition of the deposited Ti-Me-B-N thin films towards an over-stoichiometric metal content (see S1), compensated by vacancies on the non-metallic sublattice. This circumstance in itself should already increase the solubility of B, as already shown in the previous study [52]. We deliberately decided to carry out an additional series with the addition of Ti to confirm the previous results and also to be able to better describe the effect of alloying with an additional element, i.e. to better separate the two effects (vacancies on the non-metal sublattice and tuned lattice parameter). For clarity, the three series are shown in separate plots (a, b, and c), each color-coded for easy differentiation.

XRD analyses of the Ti-Me-B-N coatings reveal that each alloying series preserves the single-phase cubic face-centered cubic TiN structure consistently, without the emergence of additional crystalline (metallic) phases with increasing metal content (XRD patterns are provided in the Supplementary Materials in Fig. S1). Detailed XRD peak profile analysis gives the lattice plane distances and FWHM values of the 200-peak (d_{200} and Γ_{200}) as a function of the respective alloy content. The importance of these two parameters for the validation of a solid solution has already been proved in our previous study using HRTEM and EELS investigations [52] and is now applied here in a similar fashion. Supported by DFT calculations and extensive TEM studies, the correlation between the shifts in lattice parameters and FWHM with B solubility has been thoroughly demonstrated, showing that B solubility directly influences the microstructural changes observed in the XRD data of the films.

Starting with Fig. 4a (Ti addition), the lattice spacing increases from $d_{200}=2.134$ Å (0 at.%) with rising alloying content, reaching its maximum value ($d_{200}=2.150$ Å) by adding 2.0 at.% Ti. A further addition of Ti causes d_{200} to slightly decrease again (presumably due to vacancies on the non-metal sublattice and the slightly decreasing B-content in the coatings, see Fig. 3a-c as well as supplementary table S1, caused by the experimental setup). Simultaneously, as d_{200} increases, Γ_{200} (Fig. 4d) decreases concurrently until reaching a minimum at ~5 at.% Ti (corresponding to an amount of ~54.5 at.% Ti in the coating). A more pronounced decline in d_{200} , after an initial increase, is obtained by adding Cr (see Fig. 4b).

The maximum lattice spacing attained, reaching 2.146 Å at 1.4 at.% Cr, is below the calculated d_{200} value for fcc-Ti(N,B) with 10 at.% B in the lattice (illustrated by the dashed horizontal line). Although Cr alloying results in a minimum FWHM of the 200-peak of $\Gamma_{200} = 0.69^\circ$ at 5.1 at.% Cr, this is clearly above the minimum value of 0.35° obtained when adding Ti instead of Cr. Additionally, also the alloying range where Γ_{200} is minimal is much narrower when adding Cr. Γ_{200} rapidly

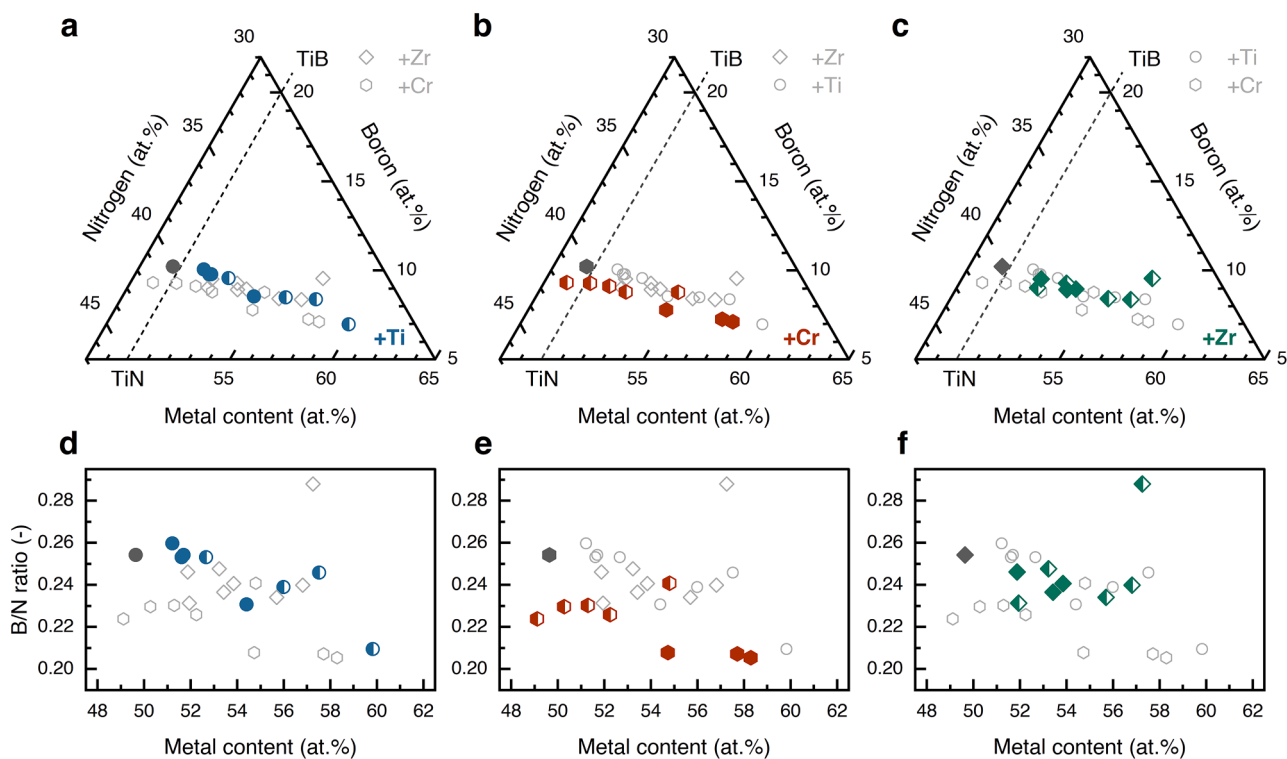


Fig. 3. (a), (b), and (c) each shows a part of the (quasi)ternary phase diagram for Ti-B-N, Ti-Cr-B-N, and Ti-Zr-B-N including the chemical compositions of the deposited samples [as determined by ToF-ERDA (coatings marked as full-filled symbols) and XRF (indicated with half-filled symbols)]. (d), (e), and (f) show the B/N ratio as a function of metal content for each corresponding alloying element. In each diagram the gray full-filled symbol (determined by ToF-ERDA) represents the TiB_{0.2}N_{0.8} coating obtained from the non-reactively sputtered TiN+TiB₂+Ti composite target. The dashed line indicates the quasi-binary TiN-TiB tie line. For clarity, the element-specific alloys are each shown in a single diagram and distinguished by color and shape: The addition of Ti is indicated by round symbols in blue, Cr by hexagonal symbols in red, and Zr by diamond-shaped symbols in green. Grey-framed symbols (within the individual panels) indicate the composition of the other alloyed coatings.

increases when adding >5.1 at.% Cr, whereas for Ti addition an increase in Γ_{200} is only observed above 10 at.% Ti. Adding Zr results in a significant increase in d_{200} and a comparatively steep decrease in Γ_{200} (Fig. 4c, f), reaching a minimum Γ_{200} by adding at least 1.8 at.% Zr. More Zr leads to a flattening of the increase in d_{200} , reaching 2.198 Å at 12.2 at.% Zr. Already with the addition of 0.7 at.% Zr the d_{200} value is 2.150 Å, thus meeting the value for a fcc-Ti(N,B) with 10 at.% B, as indicated by the intersection with the dashed horizontal line. Notably, even at alloy concentrations above 10 at.%, Γ_{200} remains small with values consistently around 0.40° .

4. Discussion

The (initial) increase in d_{200} upon alloying the TiB_{0.2}N_{0.8} coating with Ti and Cr (Fig. 4a and b) indicates that more of the available B is incorporated into the fcc-TiN lattice, because the concomitant decreasing non-metal/metal ratio as well as substitution of Ti with Cr would suggest for a decreased d_{200} , which is the case for a higher alloying content. The lattice parameter of fcc-CrN (4.15 Å) [82] is much smaller as that of fcc-TiN. When alloying TiN_{0.8}B_{0.2} with Zr, the lattice spacing continuously increases (Fig. 4c), because the substitution of Ti with Zr would also cause the lattice parameter to increase ($a_{\text{ZrN}} = 4.59$ Å [82]) and not just the promoted incorporation of B to the fcc-lattice. Consequently, for the Zr alloying case, we have two contributions for an increased lattice parameter (1: Zr substituting Ti and 2: additional B substitution of N) and one for a reduced lattice parameter (the decreasing non-metal/metal ratio like for the other two cases). A reduction of the non-metal/metal ratio (upon the addition of Ti, Cr, or Zr to TiN_{0.8}B_{0.2}) below 1 promotes the formation of vacancies at the non-metal sublattice, which also facilitates the incorporation of

additional B at the non-metal sub-lattice—in agreement with our previous results [52]. Thus, for the Zr alloying case, the separation of the two effects (1: Zr substituting Ti and 2: increasing vacancy content at the non-metal sublattice) promoting the B solubility is difficult when solely investigating d_{200} . As the N-content nearly linearly decreases with increasing Zr content, the non-metal-vacancy-induced reduction in d_{200} [83–85] as well as the Zr-for-Ti substitution-induced increase (according to Vegard's rule [86]) in d_{200} is suggested to be nearly linear as well. Thus, the positive deviation of d_{200} from such a linear slope is contributed by the additional incorporation of the provided B into the fcc-lattice.

In this regard, we complemented our XRD analysis by examining the FWHM, Γ_{200} , to strengthen the credibility of the interpretation of our results. Broader diffraction peaks (larger Γ_{200}) indicate the presence of defects, e.g., due to smaller coherently diffracting crystallite sizes caused by amorphous B-rich grain boundary phases [52,55]. Conversely, small Γ_{200} values signify a reduced degree of crystalline defects (e.g., due to larger grain sizes). Thus, small Γ_{200} further indicate for the Ti-B-N coatings a promoted solution of the provided B within the fcc-lattice. When comparing the course of Γ_{200} upon the addition of Ti, Cr, and Zr to TiB_{0.2}N_{0.8} (see Fig. 4d-f), Cr causes a less-pronounced impact and especially also a much smaller alloying range where Γ_{200} is minimum. In contrast, Γ_{200} decreases significantly—as compared to TiB_{0.2}N_{0.8} ($\Gamma_{200}=1.58^\circ$)—when adding 3–10 at.% Ti or ≥ 2 at.% Zr. Consistent with our previous findings for d_{200} [52], the combined data for d_{200} and Γ_{200} suggest that Zr addition is even more effective in incorporating the provided B into the fcc-lattice than Ti addition.

Our alloying strategy has shown that—alongside with the vacancy formation on the non-metal sublattice—the alloying element's size affects the B solubility in the fcc-TiN lattice, presumably by altering the

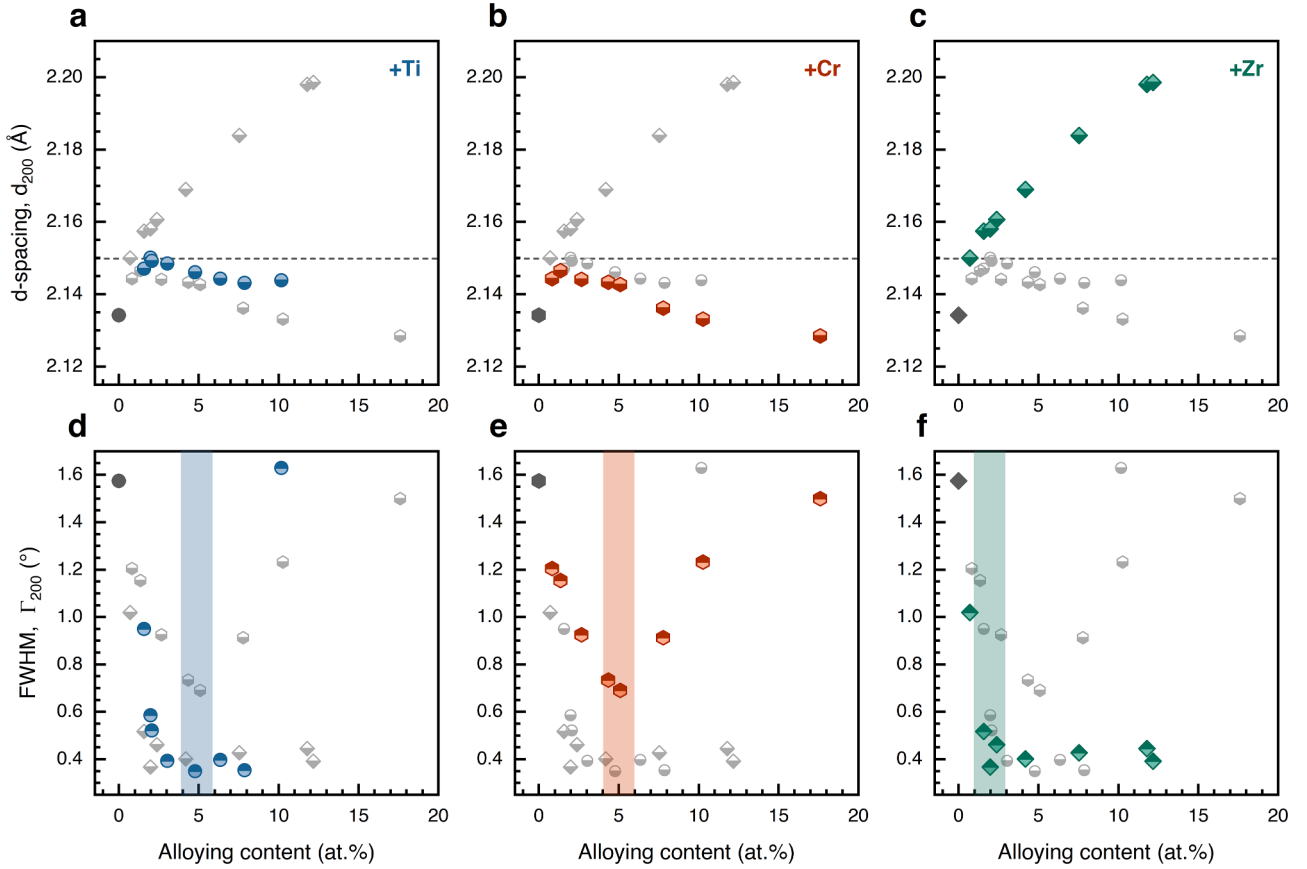


Fig. 4. (a), (b), and (c) lattice plane distances d_{200} and (d), (e), and (f) full width at half maximum (FWHM, Γ_{200}) of the 200 peaks (at $2\theta \sim 42^\circ$). Values were determined by peak profile fitting using a Pearson 7 function and an asymmetry type of peaks by split width and shape. The blue circular symbols represent the Ti–B–N coatings with incremental Ti content. The Cr- and Zr-alloyed Ti–Me–B–N coatings are represented by red hexagons and green diamonds, respectively. The gray full-filled symbol (either round, hexagonal, or diamond-shaped) represent the data point for $\text{TiB}_{0.2}\text{N}_{0.8}$. In each panel, the half-shaded gray symbols represent the other two alloyed coating series outlined in their corresponding shape. The dashed horizontal line in (a), (b), and (c) marks the ab initio DFT calculated relaxed d_{200} lattice plane distance for fcc-Ti(N,B) ($d_{200}=2.150$ Å) with 20 at.% B solved at the non-metal sublattice (see Fig. 2b). The alloy concentration range where the minimum FWHM is reached is indicated by the colored range in (d), (e) and (f).

spatial conditions for B on the non-metal sublattice. To support this reasoning, we again employ ab initio calculations to evaluate the radial distribution function (RDF) of Ti–N ($d_{\text{Ti-N}}$) and Ti–B ($d_{\text{Ti-B}}$) bonds (the nearest neighbor distance, corresponding to a local d_{200}), in the fcc-TiN_{1-x}B_x or fcc-Ti_{0.94}Me_{0.06}N_{1-x}B_x lattice. Noteworthy, there is no strain applied and all structures are fully relaxed in terms of volume, shape, and ionic positions (see Methodology). The RDF analysis allows quantifying the local misfit strains [70] in case of Me = Cr or Zr substitute for Ti at the metal sublattice.

Based on our experimental results showing improved B solubility when 2–12 at.% Zr, 3–10 at.% Ti, and ~5 at.% Cr is alloyed to $\text{TiB}_{0.2}\text{N}_{0.8}$, we did calculations of fcc-Ti_{1-y}Me_yN_{1-x}B_x supercells with $y = 0.06$ (which is equivalent to the addition of 3 at.% to the fcc-TiN lattice). By maintaining a 1:1 non-metal-to-metal ratio, our calculations focus exclusively on the size effect of the alloying element on the local misfit strain in the lattice, deliberately excluding the influence of non-metal-vacancies (which we studied previously in detail [52]). Fig. 5 shows that the local misfit strain, ϵ , almost linearly increases with increasing B content in case of fcc-TiN_{1-x}B_x, fcc-Ti_{0.94}Cr_{0.06}N_{1-x}B_x, and fcc-Ti_{0.94}Zr_{0.06}N_{1-x}B_x structures. While ϵ is initially lower for the fcc-TiN_{1-x}B_x solid solution, the fcc-Ti_{0.94}Zr_{0.06}N_{1-x}B_x structure becomes more favorable with >5.3 at.% solute B. For incorporating increasing amounts of B in fcc-Ti_{0.94}Cr_{0.06}N_{1-x}B_x, ϵ ranges between 0.94–1.40 %, thus significantly higher than in case of fcc-TiN_{1-x}B_x and fcc-Ti_{0.94}Zr_{0.06}N_{1-x}B_x. Notably, even for solving 1.6 at.% B in fcc-Ti_{0.94}Cr_{0.06}N_{1-x}B_x ($\epsilon=0.94$ %), ϵ is 15 % (relatively) higher than for

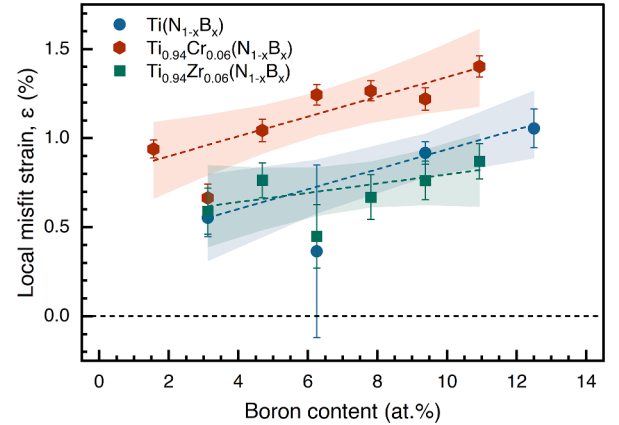


Fig. 5. DFT calculated local misfit strain ($\epsilon=(d_{\text{Ti-B}}-d_{\text{Ti-N}})/d_{\text{Ti-N}}$) as a function of the B content for three fcc-TiN structural variants: 1) fcc-TiN_{1-x}B_x (round blue-filled symbols), 2) fcc-Ti_{0.94}Cr_{0.06}N_{1-x}B_x where 6 at.% Cr substitute for Ti on the metal sublattice (hexagonal red-filled symbols), and 3) fcc-Ti_{0.94}Zr_{0.06}N_{1-x}B_x where 6 at.% Zr substitute for Ti on the metal sublattice (squared green symbols). Each calculated data point series is linearly fit and displayed with a color-coded 68 % confidence band.

the case of a fcc-Ti_{0.94}Zr_{0.06}N_{1-x}B_x solid solution with 11.0 at.% B ($\epsilon = -0.82\%$). Comparing the local misfit strains resulting from B addition in fcc-Ti_{0.94}Zr_{0.06}N_{1-x}B_x and fcc-Ti_{0.94}Cr_{0.06}N_{1-x}B_x to the basic fcc-TiN_{1-x}B_x lattice, it is evident that the Zr-substituted structure becomes most favorable with increasing B content. Although the introduction of B induces local misfit strains in all three cases (as indicated by an increase in ϵ with increasing B content), the replacement of 6 at.% Ti with larger Zr in the metal sublattice results in a less steep increase in ϵ than in the case of fcc-TiN_{1-x}B_x and fcc-Ti_{0.94}Cr_{0.06}N_{1-x}B_x. In the case of fcc-Ti_{0.94}Cr_{0.06}N_{1-x}B_x, substituting 6 at.% Ti with smaller Cr atoms in the metal sublattice already introduces local lattice strains that provide even less favorable spatial conditions for B-incorporation than fcc-TiN_{1-x}B_x.

Simplifying the situation by representing atoms as rigid spheres, we aim to illustrate how the size of alloying elements affects spatial conditions for B within the fcc-TiN lattice while also considering the effect of N-vacancies. A detailed summary concerning the data from the RDF analysis utilized for this illustration is given in the Supplementary Materials listed in Tables S2–S4.

Fig. 6a shows the fcc-TiN_{0.70}B_{0.20} lattice having 10 at.% vacancies at the non-metal sublattice. Building on our prior findings, we considered a simple model with one N vacancy added for each B atom (not necessarily in the vicinity of this B). In the fcc-TiN lattice, N occupies the octahedral interstitial site built by six Ti atoms, which themselves construct an fcc-cell. Only four of these Ti atoms are visible from the (100) plane, since the other two sit vertically, one plane above and below the N atom. Based on our calculations, the absence of an N atom induces local contractions at the metal sublattice (as seen in shorter Ti–Ti bonds listed in Table S2). In particular, the neighboring Ti atoms experience tensile strain to compensate for the missing N atom, resulting in local misfit strains. These local tensile strains caused by the non-metal vacancy, compensate—to some extent—for the compressive strain induced by the larger B atom at the non-metal sublattice. Although B substitutes for N on the non-metal sublattice, our RDF calculations do not result in significant changes in the Ti–N bond lengths (Table S2). Rather, we observe shorter (near N-vacancies) and larger (near B-atoms) Ti–Ti bonds for the introduction of B into the fcc-TiN lattice. Although non-metal vacancies compensate for some of the compressive strains induced by B, the fcc-TiN lattice expands by $\sim 1\%$ when forming an fcc-TiN_{0.60}B_{0.20} solid solution [52]. Fig. 6b illustrates the case of fcc-Ti_{0.94}Cr_{0.06}N_{0.80}B_{0.20} solid solution, where Cr and B atoms are nearest neighbors in the lattice. The substitution with smaller Cr atoms causes adjacent Ti atoms to move slightly closer together, thereby reducing the size of the octahedral sites

(or the space at the non-metal sublattice); please compare Tables S2 and S3. Consequently, the B atoms have even less space as for fcc-TiN_{0.80}B_{0.20}, consistent with our previously discussed results of Fig. 2b. As derived from DFT, the lattice parameter of fcc-Ti_{0.94}Cr_{0.06}N_{0.80}B_{0.20} (where 6 at.% Cr replace Ti), $a = 4.291 \text{ \AA}$ (calculated), is smaller than that of fcc-TiN_{0.80}B_{0.20}, $a = 4.304 \text{ \AA}$ (calculated). Compared to that, the calculated lattice parameter of fcc-Ti_{0.94}Zr_{0.06}N_{0.80}B_{0.20} is even $a = 4.329 \text{ \AA}$. However, these parameters need to be rationalized with those of the B-free lattices, TiN (4.255 $\text{\AA}$), Ti_{0.94}Cr_{0.06}N (4.247 $\text{\AA}$), and Ti_{0.94}Zr_{0.06}N (4.267 $\text{\AA}$). The data analysis suggests, as shown in Fig. 6c, that the size of the Zr atom stretches the surrounding Ti–Ti and Ti–N bonds so much that the additional B incorporation only slightly affects the lattice (see Table S3). Expanding the fcc-TiN lattice by substituting a larger Zr atom for Ti on the metal sublattice (and ZrN easily forms a solid solution with TiN) partly compensates for the local strains induced by the B atom taking the place of N at the non-metal sublattice. Conversely, replacing Ti atoms with smaller Cr atoms (also, CrN easily forms a solid solution with TiN) further restricts the spatial conditions for replacing N with a larger B atom at the non-metal sublattice. These data indicate (in combination with our previous findings on the effects of non-metal-sublattice vacancies on the B solubility) that a shared loading of the sublattices benefits the overall situation. Replacing N on the non-metal sublattice with B induces compressive strains on it. These are partly compensated by the two effects leaving the non-metal sublattice with tensile strains: 1) vacancies on the non-metal sublattice and 2) larger substitutional atoms on the metal sublattice (like Zr vs. Ti). On the contrary, replacing Ti with the smaller Cr induces compressive strains on the non-metal sublattice, which are even further increased upon the substitution of N with B.

5. Summary and conclusion

This study addresses synthesis challenges in obtaining single-phase materials of immiscible phases by overcoming spatial constraints, using Ti–B–N as model material system. First, ab initio density functional theory (DFT) calculations are employed to demonstrate the metastable nature of fcc-TiN_{1-x}B_x solid solution. By illustrating its energetic landscape in a quasi-binary convex hull phase diagram, we highlight the thermodynamic barrier that inhibits B incorporation into the fcc-TiN lattice. Our ab initio predictions further reveal the critical role of lattice strain in modulating the stability of fcc-Ti(N,B) solid solution. The models of fcc-Ti(N,B) solid solution with a tensile-strained or

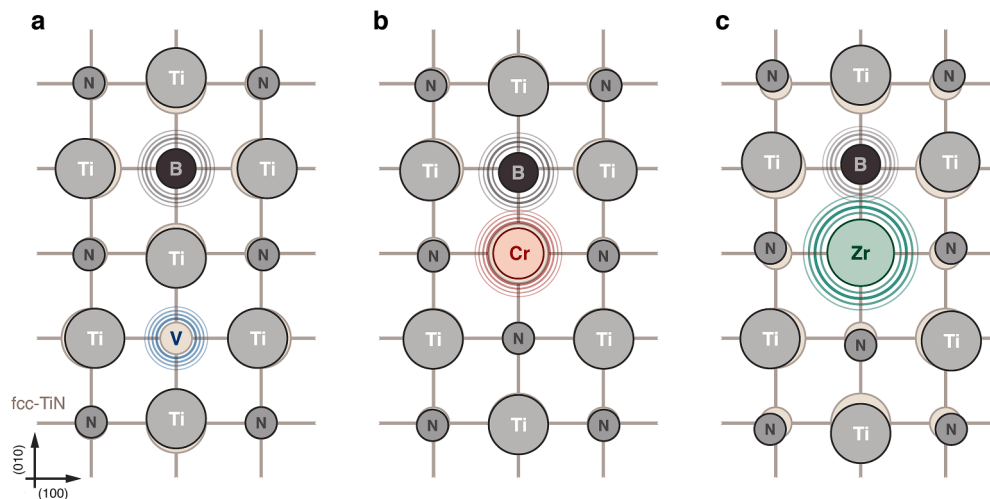


Fig. 6. Two-dimensional graphical representation of the (100) plane of (a) the fcc-TiN_{0.70}B_{0.20} lattice with 10 at.% vacancies at the non-metal sublattice, (b) the fcc-Ti_{0.94}Cr_{0.06}N_{0.80}B_{0.20} lattice, and (c), the fcc-Ti_{0.94}Zr_{0.06}N_{0.80}B_{0.20} lattice. The N vacancy as well as Cr and Zr are placed as the nearest neighbor to B. The underlying lattice construction represents the initial fcc-TiN lattice with 0 at.% B. The ratio between atomic radii [59] and bond length—based on our RDFs as listed in the Supplementary Materials in Tables S2–S4—are slightly exaggerated for clarity.

compressively-strained lattice parameter, indicate that the former can promote the incorporation of B to the non-metal sublattice. Specifically, a 1.5 % tensile strain facilitates an incorporation of up to ~28.5 at.% B. The proposed experimental microalloying approach meets with our theoretical predictions regarding the spatial constraints on B incorporation within the fcc-TiN lattice. We progressively increased the metal concentration while maintaining the B content close to 10 at% in the 25 Ti–Me–B–N coatings by adding additional Me=Ti, Cr, or Zr pieces (0–15 at%) to a Ti–B–N composite target (consisting of 50 at% Ti, 40 at% N, and 10 at% B). Although the formation of vacancies at the non-metal sublattice facilitates the substitution of N with B within the fcc-TiN lattice, the size of the metal alloying elements further defines the spatial conditions affecting the B incorporation. This observation is supported by experimental data showing that the lattice parameter increases more by alloying with Zr compared to Ti and Cr. As can be seen from the FWHM, alloying with Zr has the greatest effect on the solubility of B (the addition of only 2 at.% Zr is sufficient to fully incorporate the ~10 at.% B provided), while Cr is even less helpful than the addition of Ti. The observed slightly increased solubility of B in fcc-TiN by alloying with Cr is thus exclusively due to the resulting increased proportion of vacancies on the non-metal sublattice. This effect (due to the additional vacancies) is even lower than in the fcc-Ti(B,N) coatings alloyed with additional Ti. Notably, by alloying Ti it was possible to isolate the effect of vacancies on B solubility in the non-metal sublattice. The reduced solubility can be explained by the fact that the substitution of Ti by the smaller Cr induces additional contracting strains on the non-metallic sublattice, by which the substitution of N with the larger B becomes more difficult. Through a detailed RDF analysis we compared the local misfit strains induced by increasing the B concentration for 16 fcc-Ti_{0.94}Me_{0.06}N_{1-x}B_x structures; where Me is either Ti, Cr, or Zr. We show that the size of a larger alloying element directly affects the spatial conditions for B within the lattice, providing more space—not only through the introduction of N-vacancies—but also through an enlarged metal sublattice. In particular, when larger atoms can substitute for Ti on the metal sublattice the formation of the fcc-Ti(N,B) solid solution is favored by reducing the local misfit strain.

In summary, we introduced a novel microalloying concept aimed at manipulating the metallic sublattice to influence the solubility of B in the non-metal sublattice. By systematically introducing smaller or larger atoms into the metal lattice, we addressed the size-dependent effects of alloying atoms in forming an fcc-Ti(N,B) solid solution. The here-presented results hold promise for advancing the synthesis and design of novel materials with tailored properties and functionalities, not only within the Ti–B–N system, but also potentially in other metastable material systems.

Data availability statement

The datasets supporting this article have been uploaded as part of the supplementary material.

CRediT authorship contribution statement

Rebecca Janknecht: Writing – original draft, Visualization, Methodology, Investigation, Conceptualization. **Nikola Koutná:** Writing – review & editing, Investigation. **Katharina Weiss:** Investigation. **Eleni Ntemou:** Investigation. **Szilárd Kolozsvári:** Resources. **Paul H. Mayrhofer:** Writing – review & editing, Supervision, Project administration, Funding acquisition. **Rainer Hahn:** Writing – review & editing, Supervision, Investigation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.actamat.2024.120514](https://doi.org/10.1016/j.actamat.2024.120514).

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