Strain-stabilized Al-containing high-entropy sublattice nitrides

Andreas Kretschmer, David Holec, Kumar Yalamanchili, Helmut Rudigier, Marcus Hans, Jochen Michael Schneider, Paul Heinz Mayrhofer

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The impact of configurational entropy, enthalpy, and strain energy on the phase stability of high-entropy materials has not yet been investigated quantitatively. We used ab-initio calculations to predict the driving force for decomposition of 126 equimolar Al-containing high-entropy sublattice nitrides (HESN), which are all metastable with respect to all corresponding equimolar lower-entropy nitride phases. The entropy stabilization of $\approx -0.06$ eV/at. at 1073 K is overruled by the 0.10-0.27 eV/at. enthalpy-governed driving force for decomposition. Stabilization is however predicted for 22 compositions due to the $-0.01$ to - 0.28 eV/at. strain energy contribution caused by large differences in equilibrium volume between the HESN and their decomposition products. The predicted stabilities are consistent with diffraction and tomography data of annealed nitride coatings. Hence, it is evident that only strain enables the stabilization of the here studied Al-containing HESN, while the entropic contribution is overruled by endothermic mixing.

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1. Introduction

Since their discovery, high-entropy materials have increasingly caught attention of material scientists [1,2]. The basic principle is the random distribution of five or more elements in equiatomic or near-equatomic composition on the same crystal lattice, leading to a locally distorted lattice with high configurational entropy $S_{\text{config}} \geq 1.5 \cdot R$, $R$ being the gas constant. Four core effects have been postulated that characterize these materials, although the importance of these effects has recently been questioned [3]: high configurational entropy, distorted lattice, sluggish diffusion, and cocktail effects. Originally defined for metallic alloys, the high-entropy principle has since been expanded to ceramic materials too [4]. Since only one sublattice, which contains a fraction of all atoms, is usually occupied with chemically different species, the configurational entropy of such phases reaches $\geq 1.5 \cdot R$ only per formula unit [5]. Therefore, the name high-entropy metal-sublattice ceramics (HESC) has been coined for such materials [6].

Rost et al. [7] demonstrated the high-entropy effect in oxides, where only the metal-sublattice is occupied by five or more metal species in equiatomic or near-equatomic composition. The authors consequently claimed that configurational entropy dominates the thermodynamic landscape. However, studies on metallic alloys indicated that the impact of configurational entropy on phase stability may have been overestimated in some cases [8,9]. The controversy about whether $S_{\text{config}}$ [17], $H_{\text{Hess}}$ [10,11], or a descriptor termed “entropy forming ability” [12] defines the stability of high-entropy ceramics has not yet been addressed systematically and quantitatively.

Among the different ceramic classes, physical vapor deposited (PVD) nitrides are of great relevance in machining industries as protective thin films against wear and corrosion. PVD also represents an important synthesis route for HESC [4]. Common industry standards include (Al,Ti)N or (Al,Cr)N [13,14], which are metastable and only form solid solutions within certain chemical composition limits, which depend on various parameters [15]. The supersaturated lattices formed by PVD tend to decompose towards their thermodynamically stable phases upon thermal treatment. Typically, the mechanical properties and oxidation resistance, but also

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the mixing enthalpy (driving force for decomposition) of such coatings increase with the Al content in the cubic regime, while the formation of wurtzite-structured domains initiates the decline in the mechanical properties [16–18]. Stabilizing AlN in the cubic structure is therefore beneficial for many applications. Since high-entropy materials should benefit from sluggish diffusion and enhanced phase stability due to $S_{\text{config}}$, they are prime candidates to improve the thermal stability of Al-containing nitride coatings. Additionally, lattice strains in (TiAl)N have been proven to influence the decomposition behavior substantially [19–21]. The stabilizing potential of this effect has been proposed [11], but not yet investigated for high-entropy materials.

The discovery of new materials is aided greatly by high-throughput computations [22], since they allow efficient scanning of phase spaces that are inaccessible to experiments due to the sheer number of possible compositions. This is especially true for the field of high-entropy materials. While phase stabilities of metallic high-entropy alloys have been studied extensively by means of CALPHAD [11,23] or density functional theory (DFT) [24,25], we still lack high-throughput studies for HESC or inter-metallics, which have attracted comparatively little attention so far. Ab-initio studies have been performed on selected carbid $e$ [26–29], oxide [30–32], boride [33], nitride [6,34], and even carbonitride systems [35], but with the exception of carbides [12,29], no high-throughput studies have been published so far on HESC.

Since the exploration of the vast phase space is a daunting task, different methods – including data science approaches – have been developed to screen for possible entropy-stabilized candidates more efficiently within the framework of computational investigations [12,24,36]. While these “entropy forming ability” or “small set of ordered structures” based methods provide an efficient direction for experimental validation, they are often unable to uncover the underlying materials science. Especially the contribution of configurational entropy, claimed to dominate the thermodynamic landscape in HESC [7], remains questionable.

We have therefore investigated all equimolar Al-containing high-entropy metal-sublattice nitrides (HESN) within the phase space of the group IVb, Vb, and VIb transition metal nitrides with ab-initio simulations, to critically assess the roles of enthalpy, configurational entropy, and strain energy on phase stability. To this end, we calculated the decomposition driving forces of these solid solutions, and also of all possible decomposition products of the different multinary levels. We use the following terminology in this article: hexinary nitrides = (M1:M2:M3:M4:M5:M6)N, quintenary nitrides = (M1:M2:M3:M4:M5)N, quaternary nitrides = (M1:M2:M3)N, ternary nitrides = (M1:M2)N, and binary nitrides = MN. In reality, many other decomposition products such as non-equimolar compounds or intermetallic phases can arise, this simplification was necessary due to the sheer number of possible compositions and structures. We chose equimolar compositions since these are uniquely defined compositions for every element combination, while also maximizing the configurational entropy in the decomposition products. This allows a comparison of the relative weights of configurational entropy in the decomposition reaction. The phase space was constrained to only Al-containing HESN, since Al is paramount for resistance against oxidation, which is often limiting the performance of PVD coatings, and also for its beneficial impact on hardness. The predictions were critically evaluated with experimental thermal stability data.

2. Methods

2.1. Density functional theory

DFT calculations were performed with the Vienna Ab-initio Simulation Package (VASP) [37,38], using projector augmented plane wave (PAW) pseudo-potentials under the generalized gradient approximation [39], to study the decomposition of equimolar (AlM2M3M4M5M6)N into all possible combinations of equimolar multinary or binary nitrides. Table 1 gives a summary of all 51 possible combinations of decomposition products. For brevity, we refer to all calculated compositions, which always contain equimolar metal ratios, throughout the article with a shortened notation: (M1:M2:M3:M4:M5:M6)N or M1M2M3M4M5M6. We always stand for 20 at.% of each metal on the metal-sublattice, and a non-metal sublattice with full N-occupation. The same principle applies to the other multinary level nitrides.

The binary nitrides were calculated in the face centered cubic (fcc) B1 rock-salt structure with 1:1 stoichiometries. This represents the most stable structure at room temperature for CrN, HfN, TiN, VN, and ZrN. For the other metal nitrides their currently known most stable structures in 1:1 stoichiometry were calculated in addition. AlN was calculated in wurtzite structure (space group = SG 186) [21], MoN in NiAs-structure (SG 194) [40,41], NbN in WC-structure (SG 187) [42], TaN in hexagonal structure (SG 189) [43], and WN in NbO structure (SG 221) [44]. For the investigations of phase stability only the most stable structures were used. The structure files of all binary nitrides used, can be found in the Supplementary Material. All multinary level nitrides were calculated in B1 structure in 2 × 2 × 2 supercells with 64 atoms (32 metals, 32 N atoms). The metals were distributed on the metal sublattice by the special quasi-random structure (SQS) method to simulate random solid solutions [45]. Since 32 metallic sites do not allow for equimolar 3 or 5 component alloys, the properties of interest were obtained by averaging over 3 or 10 cells, respectively, in which the metals were permuted over the 11+11+10 or 7×7×6 d sites.

The reciprocal space was sampled with a Γ-centered Monkhorst-Pack mesh [46] with 6 × 6 × 6 k-points for all multinary nitrides. The structures, space groups, and corresponding k-meshes for the binary nitrides are listed in Supplementary Table 1. The k-mesh was chosen to give the same k-point density across all cells and dimensions. The energy-cutoff was set to 500 eV, the stopping criterion for ionic relaxation to $\approx 10^{-4}$eV. The cells were relaxed regarding size, shape, and atomic positions. We did not consider magnetism in CrN (important in CrN [47]), defects, or other structures like intermetallic compounds between the constituting metals (other than the Hagg phase to which these nitrides typically belong).

2.1.1. Phase stability

The driving force $\Delta G_{\text{mix}}$ of a mixing reaction A + B $\rightleftharpoons$ AB is composed of enthalpy and entropy contributions:

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}}$$  

where a negative value of $\Delta G_{\text{mix}}$ indicates a stable mixture AB and a positive value decomposition into the constituting phases A and B.

The consideration of only equimolar solid solutions as decomposition products ignores many other possible phases like non-equimolar structures, which can be energetically favorable despite their lower configurational entropy. As such, the equimolar systems selected for analysis in this paper may not always correspond to the points of local energy minima in the analyzed composition space. A full treatment of all possible decomposition products is not feasible at the moment for such a large phase space due to the sheer number of possible compositions and structures involved. We chose equimolar compositions since these are the only uniquely defined compositions for every element combination, while also maximizing the configurational entropy in each. Since our study focuses on the role of configurational entropy in
such decomposition reactions, we limited the scope of our paper to these phases.

\[ \Delta H_{\text{mix}} = \Delta H_{f,\text{product}} - \sum_i v_i \Delta H_{f,i} \]  

(2)

\( E_f \) being the energy of formation of the product or of the ith educt and \( v_i \) being the stoichiometric coefficient of the reaction for the ith educt. \( E_f \) is calculated as [48]

\[ E_f = \frac{1}{\sum_i n_i (E_{\text{tot}} - \sum_i n_i \mu_i)} \]

(3)

with \( E_{\text{tot}} \) being the total energy of the supercell, \( n_i \) and \( \mu_i \) the number of atoms and the chemical potential of the ith species. The chemical potentials of the elements are calculated as the total energy per atom of the respective ground state structures: face centered cubic (Al), body centered cubic (Cr, Mo, Nb, Ta, V, and W), hexagonal close packed (Hf, Ti, and Zr), and the N\(_2\) molecule. The mixing entropy, \( \Delta S_{\text{mix}} \), is calculated as the difference in configurational entropy between the product and the educt phases:

\[ \Delta S_{\text{mix}} = S_{\text{config, product}} - \sum_i v_i S_{\text{config, i}} \]

(4)

Other entropy contributions such as vibrational, magnetic, and electronic entropy can be expressed in selected systems [49,50] but are not feasible for high-throughput computing at the moment due to the sheer computational expense involved and are thus not considered here. The non-metal sublattice is perfectly ordered so that the nitrogen-atoms do not contribute to configurational entropy. Only the metal-sublattice is randomly occupied, so that the configurational entropy (per atom) for our 1:1 metal-nitrides is calculated as

\[ S_{\text{config}} = -k_B \frac{1}{2} \sum_i X_i \ln X_i \]

(5)

with \( k_B \) being the Boltzmann constant, and \( X_i \) being the mole fraction of the ith component in the solid solution. Since all compositions are equimolar, a simplified formula can be applied:

\[ S_{\text{config}} = \frac{1}{2} k_B \ln N \]

(6)

where \( N \) is the number of elements on the metal-sublattice. The entropy contribution was calculated for 0 and 1073 K. The volume change during decomposition of our heximary nitride was calculated as

\[ \Delta V = \sum_i v_i V_i - V_{\text{product}} \]

(7)

with \( V_i \) and \( V_{\text{product}} \) being the volumes of the ith educt and the product, respectively. The elastic properties of predicted stable decomposition products were calculated with the stress-strain method [51] from their structurally relaxed cells. The elastic constants were then projected onto cubic symmetry with the method of Moakher and Norris [52]. The bulk modulus was calculated as average of the Reuss and Voigt estimates [53]:

\[ B = \frac{B_R + B_V}{2} \]

(8)

\[ B_V = \frac{(C_{11} + C_{22} + C_{33}) + 2(C_{12} + C_{13} + C_{23})}{9} \]

(9)

\[ B_R = \frac{1}{(S_{11} + S_{22} + S_{33}) + 2(S_{12} + S_{13} + S_{23})} \]

(10)

where \( c_{ij} \) and \( s_{ij} \) are the matrices of elastic constants and compliances, respectively.

The strain energy for the isstructural decomposition was calculated with the Birch-Murnaghan equation of states [54]:

\[ E_{\text{tot}}(V) = E_0 + 9V_0 B_0/16 \left[ (V_0/V)^{2/3} - 1 \right]^3 B_0' + \left[ (V_0/V)^{2/3} - 1 \right]^2 \left[ 6 - 4(V_0/V)^{2/3} \right] \]

(11)

where \( V_0 \) is the equilibrium volume, \( B_0 \) is the bulk modulus at \( V_0 \), \( E_0 \) is the equilibrium energy at \( V_0 \), \( B_0' \) is the derivative of the bulk modulus with respect to pressure, and \( E_{\text{tot}}(V) \) is the total energy at the desired volume \( V \). We followed the strategy of refs. [20,21], namely assuming that the decomposition products A and B (now considering the mixed phase as educt) have to take the same volume as the parent phase AB (which is assumed to be in a stress-free state). Therefore, we have evaluated the energy difference between the ith product’s equilibrium energy (total energy at equilibrium volume \( V_{0,i} \)) and its total energy at equilibrium volume \( V \) of the parent phase AB using the Birch-Murnaghan equation of states as:

\[ E_{\text{strain},i} = E_{\text{tot},i}(V) - E_{\text{tot},i}(V_{0,i}). \]

(12)

This strain energy was added to the formation energy \( E_{f,i} \) in Eq. (2) to account for the strain effects. Since the equilibrium structures were calculated by automatic full structural optimizations, relaxing atomic positions, cell shape, and volume, we did not calculate explicit values of energies at different volumes. We therefore do not know the exact value of \( B_0' \) in our compositions, and instead assumed \( B_0' = 4 \) in all cases [55–57].

2.1.2. Structure analysis

The variation of bond lengths in the relaxed structures was analyzed by a radial distribution function, \( rdf(r) \), representing a density of atoms at a spherical ring with radius \( r \) and thickness \( dr \) from an atom. Thereby, its peaks correspond to coordination shell radii, which were fitted with Gauss distributions:

\[ rdf(r) = a_i \cdot e^{-\frac{(r-r_0,i)^2}{2\sigma_1^2}} \]

(13)

with \( r_0,i \) being the mean bond length (for the ith peak), \( a_i \) being a fitting parameter, and \( \sigma_1^2 \) the variance in atomic bond lengths. The values of \( \sigma_i \) were plotted against the average nominal bond

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<table>
<thead>
<tr>
<th>Table 1</th>
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<tbody>
<tr>
<td>Calculated decomposition scenarios for the 126 heximary nitrides ((M_1M_2M_3M_4M_1)_N) considered here. These nitrides are all possible heximary combinations of AlN with Vi, Vb, and Vb transition metal nitrides. For example, there are 5 possible combinations of the decomposition products for the reaction ((M_1M_2M_3M_4M_1)_N \rightarrow (M_1M_2M_3M_4)_N + M_1N), etc.</td>
</tr>
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<table>
<thead>
<tr>
<th>Combinations</th>
<th>Product 1</th>
<th>Product 2</th>
<th>Product 3</th>
<th>Product 4</th>
<th>Product 5</th>
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<tbody>
<tr>
<td>1</td>
<td>((M_1M_2M_3M_4)_N)</td>
<td>(+M_1N)</td>
<td>(+M_2N)</td>
<td>(+M_3N)</td>
<td>(+M_4N)</td>
</tr>
<tr>
<td>2</td>
<td>((M_1M_2M_3M_4)_N)</td>
<td>(+M_1N)</td>
<td>(+M_2N)</td>
<td>(+M_3N)</td>
<td>(+M_4N)</td>
</tr>
<tr>
<td>3</td>
<td>((M_1M_2M_3M_4)_N)</td>
<td>(+M_1N)</td>
<td>(+M_2N)</td>
<td>(+M_3N)</td>
<td>(+M_4N)</td>
</tr>
<tr>
<td>4</td>
<td>((M_1M_2M_3M_4)_N)</td>
<td>(+M_1N)</td>
<td>(+M_2N)</td>
<td>(+M_3N)</td>
<td>(+M_4N)</td>
</tr>
<tr>
<td>5</td>
<td>((M_1M_2M_3M_4)_N)</td>
<td>(+M_1N)</td>
<td>(+M_2N)</td>
<td>(+M_3N)</td>
<td>(+M_4N)</td>
</tr>
</tbody>
</table>
length difference between the metal and non-metal sublattice $\delta$, calculated as

$$\delta = \sqrt{\sum_{i=1}^{N} x_i \left(1 - \frac{r_i}{r_f}\right)^2}$$

(14)

with $x_i$ being the mole fraction of the $i$th component, $r_i$ the nearest neighbor $N$-metal bond length of the $i$th metal, and $r_f$ the average nearest neighbor $N$-metal bond length of all metals present [58].

The bond lengths were calculated from the relaxed fcc-structured binary nitrides, the relevant values are listed in Supplementary Table 2.

2.2. Deposition

Coatings of the material systems (Al,Cr,Nb,Ta,Ti)N, (Al,Hf,Ti,V,Zr)N, (Al,Hf,Mo,V,Zr)N, and (Al,Mo,Ta,V,W)N were deposited by reactive magnetron sputtering in a modified Leybold Heraeus Z400 facility from powder-metallurgically prepared equiatomic 75 mm-diameter targets of the corresponding metals (Plansee Composite Materials GmbH). (100)-oriented Si (20 × 7 × 0.38 mm³) and (1102) sapphire (10 × 10 × 0.53 mm³) substrates were coated, mounted face-to-face to the target at a distance of 4 cm, with a bias potential of −50 V DC and at a deposition temperature of 440 °C.

After reaching a base pressure of 0.3 mPa, the substrates were Ar-ion etched at a pressure of 1.3 Pa for 15 min by applying a negative pulsed DC substrate potential of −150 V with a pulse frequency of 150 kHz and a pulse duration of 2496 ns. The targets were cleaned prior to deposition by sputtering for 2 min behind the closed shutter. A 18 sccm/22 sccm gas mixture of N₂/Ar (both 99.999% purity) at a pressure of 0.43 Pa was used for all depositions. The cathode was operated with a constant current of 0.75 A.

2.3. Sample characterization

Chemical compositions were obtained from coatings on Si substrates by energy dispersive X-ray spectroscopy (EDS) using a PANalytical X'Pert Pro-MPD (θ–θ diffractometer) equipped with a Cu-κα source ($\lambda = 0.15408$ nm, 45 kV and 40 mA) in Bragg-Brentano geometry. Indentation hardness, $H$, and indentation modulus, $E$, of the coatings were measured before and after the annealing process on coated sapphire substrates using an UMIS II nanoindenter. The procedure by Oliver and Pharr [59] was used to analyze the load-displacement curves.

The nanometer-scale composition of thin films in as-deposited state and after annealing treatment at 800 °C for 30 h was characterized by atom probe tomography (APT). A CAMECA local electrode atom probe 4000X HR was employed and field evaporation was assisted by laser pulses at 125 kHz frequency, 60 K base temperature and 1.0% average detection rate. Based on the electric field strength-dependent measurement accuracy of laser-assisted APT for (Ti,Al)N, the laser pulse energy of 10 pJ was used [60]. 30 million ions were collected in each measurement, data analysis was carried out with IVAS 3.8.6 and the shank angle protocol was used for the reconstructions. Needle-like specimens were prepared in a FEI Helios Nanolab 660 dual-beam microscope by focused ion beam techniques using a standard protocol [61]. Low voltage specimen cleaning was done at 5 kV and 40 Pa for 30 s.

3. Results and discussion

3.1. Density functional theory calculations

3.1.1. Phase stability

Fig. 1 shows a stability landscape of all here investigated 126 HESN (rows) into their most stable decomposition products (columns) at 0 K, considering only enthalpic effects since $T \Delta S = 0$. Only the reaction with the highest driving force (maximum $\Delta H_{\text{mix}}$) out of the possible 51 combinations (see Table 1) is displayed for each hexinary nitride. The colored squares indicate which phases are predicted to form out of the respective HESN, the color indicates the driving force $\Delta G_{\text{mix}}$ (here only $\Delta H_{\text{mix}}$) of the reaction in eV/at. Additionally, the experimentally tested compositions are highlighted in red. The parent phases are sorted by increasing driving force from bottom to top, while the decomposition products are grouped by their multinary levels (MN to (M₃,M₂M₃M₂N) and then alphabetically. White squares mean that either a different decomposition reaction is more likely (higher $\Delta G_{\text{mix}}$), or that one or more occurring elements do not match the parent phase. The box on the left marks the elements present in each corresponding row (except Al and N). For example, in the topmost row (Al-MoNbTaW)N is predicted to decompose into each binary nitride, the driving force for this reaction is $\approx 0.27$eV/at. Other reactions, such as the decomposition into a combination of some binary and ternary nitrides, possess a lower driving force and are therefore not shown.

From a purely energetic point of view, decomposition is expected to take place in all compositions. The main cause for this is the separation of AlN, which is predicted to form in all cases (colored squares in the leftmost column for all rows). The lowest driving force for decomposition (equal to $\Delta G_{\text{mix}}$) with 0.10 eV/at. shows (AlCrHfTi)N, the highest $\Delta G_{\text{mix}}$ with 0.27 eV/at. shows (Al-MoNbTaW)N. The occurrence of the different elements sorted by driving force (left box) shows interesting patterns for Cr and W, while the other elements are more randomly dispersed across the range of the energy landscape. While Cr is present only in compositions that exhibit $\Delta G_{\text{mix}} < 0.215$eV/at., meaning it is not present in compositions with the highest driving forces, W shows the opposite behavior. The consideration of the magnetic ground-state of CrN would shift the $\Delta G_{\text{mix}}$ values up. All W-containing compositions show a $\Delta G_{\text{mix}} > 0.151$eV/at.. This is an indication that especially W is not compatible in solid solutions with a 1:1 stoichiom-
etry without vacancies (as considered here). This can be explained by the mechanical and thermodynamic instability of WN in fcc structure [44] (positive $E_I$ in 1:1 fcc structure, and $\approx -0.4\text{eV/at.}$ in the stable NBO-structure). Interestingly, MoN does not show this trend even though its stability is comparable to WN ($E_I$ very close to 0 and $\approx -0.4\text{eV/at.}$ for the 1:1 fcc and the stable hexagonal structure, respectively, compare [62]). This could be due to the comparatively lower volume mismatch between the fcc and hexagonal MoN phases.

The mixing enthalpy of ($\text{AlCrNbTiV})\text{N}$ was calculated in [34] to be 0.06 eV/at., which is significantly lower than the 0.12 eV/at. calculated here. Among other reasons such as different calculation settings and treatment of magnetic disorder, this is due to the choice of decomposition products. While AlN was correctly treated in its wurtzite structure in [34], the $E_I$ of NbN in the fcc structure is also significantly higher than in its thermodynamically more stable hexagonal WC-structure (being considered here). Also, even at 0 K, the ternary compound (CrV)$\text{N}$ is predicted to be favored over CrN+VN, leading to a comparatively higher driving force for decomposition towards their most stable products, which includes also possible ternary or other multinaries and not the binaries alone. From the $\Delta H_{mix}$ of 0.06 eV/at. the authors estimated that the entropic-benefit at temperatures above 727 °C stabilizes ($\text{AlCrNbTiV})\text{N}$ against decomposition. However, the experimental validation [34] showed that this material did indeed decompose, meaning that the postulated decomposition path was too optimistic.

So far only enthalpic effects were considered. By including $T \cdot \Delta S_{mix}$ to the phase stability, the overall picture changes slightly. The maximum entropy stabilization for a decomposition into binary nitrides is $6.9 \times 10^{-2}\text{eV/(at.}\cdot K)$. Fig. 2 shows the same kind of stability landscape as Fig. 1 but with an entropy contribution at 1073 K. While in theory we can use any higher temperature to reach entropy stabilization eventually, the thermal stability of nitrides imposes practical limits. For example, Cr, Ta, and V are reported to lose nitrogen at temperatures above 900 °C [63–65], while binary MoN and WN are unstable in their 1:1 stoichiometry [41,44,62,66]. Hence, as N-loss is not implemented in the computational strategy employed here, 800 °C = 1073 K was selected for the calculations as well as for the annealing experiments.

Even with the contribution of configurational entropy, all compositions are predicted to decompose into AlN and other phases. On average, the driving force decreases by 0.065 ± 0.007 eV/at., a minimum driving force of $\Delta G_{mix} \approx 0.053\text{eV/at.}$ is now calculated for ($\text{AlCrHfTi})\text{N}$, while AlMnO+NbTaW+N shows - like at 0 K - the highest driving force of now $\approx 0.192\text{eV/at.}$ The distribution of elements along the sequence of $\Delta G_{mix}$ changes very little with the added entropy contribution. W leads to the highest driving forces for decomposition, while Cr tends to lead to lower $\Delta G_{mix}$. Although configurational entropy does not prevent nucleation and growth of AlN, it does change the nature of the most likely decomposition products to include nitrides with more configurational entropy. For example at 0 K ($\text{AlCrHfTi})\text{N}$ is predicted to decompose into AlN+HfN+TiN+(CrV)$\text{N}$, while at 1073 K the formation of AlN+($\text{CrHfTi})\text{N}$ is preferred. Since this quaternary nitride also contains considerable configurational entropy – 1.39 $\cdot$ R on the equiatomic metal-sublattice – it profits from the $\Delta S_{mix}$ and therefore becomes more favored as decomposition product at higher temperatures. The same is true to a lesser extent for ternary and quaternary nitrides. At 0 K, only four ternary nitrides are predicted to form: (CrHf)$\text{N}$, (CrTi)$\text{N}$, (CrV)$\text{N}$, and (HfZr)$\text{N}$. At 1073 K, 9 ternary, 2 quaternary, and 2 quinventary nitrides are among the most stable decomposition products, so while we cannot attest entropy stabilization to any of the investigated HESN, we see this stabilization in a few lower-entropy nitrides without Al at temperatures where decomposition reactions are kinetically able to take place. The entropy stabilization causes some of the compositions to change place in the $\Delta G_{mix}$-sequence. Those educts, which are predicted to form products with more entropy, are found in the lower part of Fig. 2 (low driving force), while the compositions at the upper end of $\Delta G_{mix}$ form mostly binaries and occasionally a ternary nitride.

### 3.1.2. Strain stabilization

In addition to energetic and entropic effects, volume mismatch of the decomposition products can also influence the decomposition process significantly [19–21]. In all cases considered here, the decomposition products have between 1.3% (($\text{AlCrNBZr})\text{N}$) and 8.1% (($\text{AlCrMoTaW})\text{N}$) larger volumes than their parent phases, see Supplementary Fig. 1 for a detailed overview. This is partly also due to the much larger volumes of some binaries in their thermodynamically more stable structure, like AlN. The distribution of elements in the compositions in the $\Delta V$-sequence is different to the ordering by $\Delta G_{mix}$, mostly due to the different structure types in the binary nitrides. Ta and especially W are concentrated in compositions with large mismatch. This is due to their much larger volumes in their most stable structures compared to their fcc cells: TaN has a 6.3% larger volume in its hexagonal structure, and WN a 12.3% larger volume in its NBO-structure compared to the respective fcc cells. For comparison, the fcc volumes of MoN and NbN are 1.0 and 3.0% larger than in their stable structures, respectively, while for AlN the wurtzite structure has a 20.1% larger volume than the fcc phase, causing a large activation energy barrier in Al-containing transition metal nitrides [13]. This means that while from an energetic point of view the driving force for decomposition is high in all investigated compositions, the volume mismatch can hinder the decomposition. Additionally, what is not considered here is that decompositions would also require the formation of interfaces, which further consumes energy [19].

Fig. 3 depicts the stability landscape of most likely decomposition reactions at 0 K with added strain stabilization, calculated from the volume mismatch and the bulk modulus of all decomposition products. 22 compositions show a negative $\Delta G_{mix}$, indicating potential for sufficient strain stabilization against decomposition. Among the stable compositions Cr and V are common, which are absent in the upper part of the stability landscape (representing a high driving force for decomposition). This is due to a combination of comparatively lower driving force in such compositions without stabilizing effects, and high bulk moduli (see Table 2). Although we only considered non-magnetic CrN, which leads to an overestimation of the strain energy due to a much larger $B$ than reported for paramagnetic CrN [67,68], we can conclude from repeated calculations with $B_C = 250\text{GPa}$ that there is only a negligible influence ($\approx 0.001\text{eV/at.}$ difference on average) by this parameter. Mo and Nb on the other hand are present in only 3 and 2 strain stabilized compositions, respectively, and are common in many compositions with high $\Delta G_{mix}$.

### 3.1.3. Distribution of bond lengths

Atomic radii represent size trends poorly in ceramics, as shown in [69] for borides, where the lattice constants of metal diborides were used instead. Since ceramics have different chemical behavior than metals, the size trends between metals do not generally agree with the size trends between the ceramics formed by these metals. Therefore, we use the nearest neighbor metal-nitride bond lengths (from fcc binary nitrides) to evaluate the size differences $\delta$ between individual nitrides.

Fig. 4 shows the relationship between $\delta$ and $\sigma_1$, the parameter from the radial distribution function for the first coordination sphere, indicating the spread of nearest neighbor bond lengths. In all binary nitrides, $\sigma_1$ and $\delta$ are 0. In nitrides with differently sized
Fig. 1. Stability landscape of the most likely decomposition products at 0 K (no entropy contribution). The 126 hexinary nitrides are sorted by the driving force $\Delta G_{\text{mix}} = \Delta H_{\text{mix}}$. Only 4 ternary nitrides, (CrHf)N, (CrTi)N, (CrV)N, and (HfZr)N, are predicted to form next to the binary nitrides. No composition is predicted to be stable against decomposition, and w-AlN is always predicted to form together with other phases. The left box indicates the metals present in each educt. The maximum, minimum, and average $\Delta H_{\text{mix}}$ of all compositions are marked on the scale. The four highlighted compositions (marked in red) were tested experimentally. For easier reading we refer to the individual nitrides without the parentheses, all have a N/Me ratio of 1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 2. Stability landscape of the most stable decomposition products at 1073 K. The added contribution by 1073 K $\Delta S_{\text{mix}}$ changes the stability landscape at 0 K Fig. 1 only little, indicating that the configurational entropy has only a small impact on $\Delta G_{\text{mix}}$, for these ceramic materials with their typically high enthalpy. Compared to 0 K, the number of favorable products increases to include 9 ternary, 2 quaternary, and 2 quintenary nitrides, which become entropy stabilized against their binary nitrides. The left box shows clustering of the metals along the $\Delta G_{\text{mix}}$ axis. The maximum, minimum, and average $\Delta G_{\text{mix}}$ of all compositions are marked on the scale. The four highlighted compositions (marked in red) were tested experimentally. For easier reading we refer to the individual nitrides without the parentheses, all have a N/Me ratio of 1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
Fig. 3. Stability landscape at 0 K like in Fig. 1, but with strain energies considered. These evolve upon decomposition due to the different specific volumes between decomposition products and their parent phases. The strain energies obtained by the Birch-Murnaghan equation of states show a more pronounced influence on the stability landscape than the configurational entropy, compare Figs. 1 and 2. 22 compositions are predicted to be stabilized by strain energy (being in the range 0.01-0.28 eV/\text{at.}). The average decrease of $\Delta G_{\text{conf}}$ by strain is $\approx 0.12$ eV/\text{at.}\). The left box shows the clustering of metals along the $\Delta G_{\text{conf}}$ axis and provides insights on stability trends. The maximum, minimum, and average $\Delta H_{\text{mix}}$ of all compositions are marked on the scale. In the strain stabilized materials, Cr and V are the most common elements, they are also absent in the compositions with the highest driving forces for decomposition. The four highlighted compositions (marked in red) were tested experimentally. They were selected based on the criteria of being stabilized by strain alone, in the case of (Al,Hf,Ti,V,Zr)\text{N}, and being potentially stabilized when considering also entropic contributions \((\text{Al},\text{Cr},\text{Nb},\text{Ta},\text{Ti})\text{N}\), (Al,Hf,Mo,V,Zr)\text{N}, and (Al,Mn,Mo,V,Zr)\text{N}. For easier reading we refer to the individual nitrides without the parentheses, all have a N/Me ratio of 1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

metals, a correlation between $\sigma_1$ and $\delta$ can be seen. A linear fitting function is displayed as guide, but the calculated $R^2$ score of 0.65 indicates only a moderate correlation. The multinary level of the nitride plays no significant role in this relationship, so that the highest bond length differences of 5–6% in (AlZr)\text{N} or (CrZr)\text{N} lead to the highest values of $\sigma_1$. This means that the high lattice distortion, which is supposed to be a characteristic core effect in high-entropy materials, is directly achieved by the differently sized metals rather than by the number of different species alone.

The HESN do form a cluster at the upper part of the plot, but this is in part due to the constraint of always having Al present in these nitrides, which is the element with the smallest metal–N bond length of the here considered fcc-nitrides. VN and CrN have slightly longer bonds, while the other metal nitrides show significantly larger bond lengths (see Supplementary Table 2). When expanding the phase space to Al-free hexinary nitrides, the smallest $\delta$ of 1.4% would be reached in (HfMoNbTaW)\text{N}, presumably accompanied by a correspondingly low $\sigma_1$.

Since lattice distortion and the corresponding sluggish diffusion have been reported to be central to the high-temperature properties of high-entropy materials numerous times [6,70–72], we postulate that the lattice distortion should not be taken for granted in HESC. The material selection should also encompass the size of the constituents in the respective chemical setting. This is further supported by Ref. [73], reporting that the diffusion in several medium- and high-entropy alloys depends strongly on the presence of Mn.

3.1.4. Limitations

Since the SQS cell size is rather limited, the impact of individual configurations on the total energy should be estimated. For that end, we calculated three additional newly generated cells for six compositions that were picked based on the difference in total energies between the ten individual cells. The three compositions with the smallest differences, (AlCrTiVZr)\text{N}, (AlCrMnTiZr)\text{N}, and (AlCrMoVZr)\text{N}, and the three compositions with the largest differences, (AlHfMoTaZr)\text{N}, (AlCrHfTaW)\text{N}, (AlCrHfTaZr)\text{N} were chosen. All of the calculated cells are in excellent agreement with the originally used cells (with identical metal occupation). The standard deviation of the total energy between the now four cells is only 0.007 eV/\text{at.} or less in all cases. This means that differences

Fig. 4. Radial distribution function for the first coordination sphere, $\sigma_1$, $\sigma_2$ indicates the spread of nearest neighbor bond lengths in relation to the nearest neighbor metal-nitride bond lengths $\delta$ for the individual binary, ternary, quaternary, quinternary, and Al-containing hexinary nitrides considered here. A linear fit is shown as guide, but the correlation is only moderate. For easier reading we refer to the individual nitrides without the parentheses, all have a N/Me ratio of 1.
in total energy between the individual cells (ranging between 0.10 and 0.17 eV/atom) stem from the slightly different metal occupations and not from the geometrical arrangement. We can therefore confidently state that our simulation of a solid solution by SQS is accurate enough for our purpose.

The choice of calculating the elastic properties with the strain-stress method left us with no information on $B'_0$, so that we estimated the value $B'_0 = 4$ from literature [55–57]. This approach was validated with energy-volume fittings using Eq. (11) to calculate $B'_0$ for AlN, HfN, TiN, and WN (all in their stable structures). The respective values are 3.71, 3.55, 4.24, and 4.79. In addition, we also calculated the mixing enthalpies with strain component with $B'_0 = 3$ and 5 to demonstrate that this parameter is of little importance within this range. On average, this change in $B'_0$ leads to a change of $-0.004$ eV/atom, in $\Delta G_{\text{mix}}$, so that only border cases of strain stabilization would be affected, leading to 18 or 24 strain stabilized compositions at $B'_0 = 3$ and 5, respectively (22 stable compositions at $B'_0 = 4$). The mixing enthalpy of (AlHfTiVZr)N for example is $-0.004$ eV/atom at $B'_0 = 4$ and changes to $-0.002$ eV/atom at $B'_0 = 3$ and $-0.006$ eV/atom at $B'_0 = 5$.

By accounting for strain stabilization, the driving force for decomposition decreases on average by 0.118 ± 0.051 eV/atom, which is much higher than the $\sim 0.06$ eV/atom. entropy contribution at 1073 K, shown in Fig. 2. By combining both effects, a larger list of stabilized compositions could be obtained, but a clear threshold value cannot be given here, since the strain stabilization is only known at 0 K, while the entropy contribution comes into play at high temperatures like 1073 K. The temperature-dependence of lattice parameters and elastic constants can be calculated with ab-initio methods [74–76], but this is prohibitively expensive on such a large number of compositions. Also, other entropy contributions like vibrational, magnetic, and electronic entropy can influence the properties significantly. In the so-called “Cantor-alloy”. CoCr-FeMnNi, these contributions can amount to 50% of the configurational entropy [49]. Such effects could not be considered here, because there is currently no method accessible for high-throughput calculations.

The here considered non-magnetic fcc-CrN and fcc-VN are both dynamically unstable [47,77], but our data are in agreement with calculations on (Al,Cr)N and (Al,V)N (considering the correct magnetic situation and reference state), which show considerably smaller mixing enthalpies than (Al,Ti)N [78,79]. We therefore expect only a small uncertainty in our calculations that would not change the overall picture when using a different reference state. Since this study considers only fully relaxed solid solutions, whereas in PVD coating microstructures compressive stresses due to growth defects are common, the results need to be treated with care when interpreting experiments.

Based on our calculations, four compositions were chosen for experimental validation: (Al,Hf,Ti,V,Zr)N, predicted to be already stabilized by strain alone ($\Delta G_{\text{mix}} = -0.005$ eV/atom), as well as (Al,Hf,Mo,V,Zr)N ($\Delta G_{\text{mix}} = 0.023$ eV/atom), (Al,Cr,Nb,Ta,Ti)N ($\Delta G_{\text{mix}} = 0.036$ eV/atom), and (Al,Mo,Ta,V,W)N ($\Delta G_{\text{mix}} = 0.055$ eV/atom), which are predicted to decompose.

3.2. Experimental validation

3.2.1. Chemistry and phase formation

The chemical compositions of our as-deposited coatings on Si substrates, analyzed with EDS, are shown in Table 3. All coatings are under stoichiometric to some extent, which is most pronounced in (Al,Mo,Ta,V,W)N. This can be explained with the tendency of all the comprising metals except for Al to form N-vacancies in their cubic structures [6,41,44,62,64,66]. Using equimolar targets, higher concentrations of the heavier elements and a lower Al content are obtained, which is typical for sputtered materials due to different poisoning states of the individual target grains [80,81] or due to preferential gas-scattering and resputtering of AlN [82,83]. Additionally, the quantification of light elements in EDS is uncertain due to absorption of X-rays in the sample and the spectrometer [84]. Since Al is the largest contributor in driving force for decomposition, but also for strain stabilization, we need to consider this deviation from equimolarity when interpreting the results.

Fig. 5(a) and (b) show the XRD patterns of our coatings as-deposited and after annealing at 800 °C for 30 h, respectively. This temperature was chosen to match the 1073 K used in our simulations, and also because we have to balance the thermal stability of the nitrides with the slow kinetics in high-entropy materials. Since N-loss occurs in nitrides at high temperatures, this would lead to the formation of additional phases, which complicates the comparison with our DFT data. In addition, the adherence of (Al,Mo,Ta,V,W)N on sapphire was insufficient at 850 °C and above. The long annealing time of 30 h (≤1 h is common for thin films) was chosen to account for the slow diffusion processes in high-entropy materials (one of the four core-efforts [6,32,85,86]).

All coatings show single-phase fcc-rock-salt structures in their as-deposited state. The (Al,Cr,Nb,Ta,Ti)N, (Al,Hf,Ti,V,Zr)N, and (Al,Hf,Mo,V,Zr)N exhibit a similar pronounced (220) growth orientation, with smaller (200) and (311) reflexes, and very small (111) peaks in the case of (Al,Hf,Ti,V,Zr)N and (Al,Hf,Mo,V,Zr)N. (Al,Mo,Ta,V,W)N on the other hand exhibits a pronounced (200) growth orientation. These preferred growth orientations remain unchanged by the thermal treatment for all coatings studied. The only notable change for (Al,Hf,Ti,V,Zr)N (Fig. 5, bottom pattern) is a slight narrowing of the individual peaks, indicative for structural recovery effects, where lattice-defects rearrange towards lower energy sites. No N-loss, or formation of a secondary phase could be detected. This corresponds well to the predicted strain stabilization of this material.

The (Al,Mo,Ta,V,W)N is still highly (200) oriented (Fig. 5, second pattern from bottom) after annealing, but the peak shifts from 42.33 to 43.07 °. This reduction in lattice plane distances is typically indicative for reduced stresses (macro-stresses), but would go hand-in-hand with a reduction of peak broadening (micro-stresses) as well. However, the full width at half maximum (FWHM) of the (200) peak increases from 0.54 to 0.89 °. Therefore, in combination with DFT (Mo,N, Ta, and WN are prone for N-loss [48,62,87]), this pronounced peak-shift suggests a reduced lattice size due to N-loss of the fcc structure. At diffraction angles of around 59 ° and 68 ° two additional very broad and small features can be detected after the annealing treatment, but no crystalline phase could be unambiguously assigned. We do not see formation of w-AlN, which can be due to the comparably low Al concentration. Of all the coatings investigated, this (Al,Mo,Ta,V,W)N deviates most from the equimolar composition that was used for DFT. Additionally, the N-loss could also stabilize the nitride in its fcc structure. While these features are hints for decomposition reactions, XRD remains inconclusive in this case.

For the (Al,Hf,Mo,V,Zr)N coating (Fig. 5, third pattern from bottom), the (220) XRD peak becomes asymmetric upon annealing due to a possible formation of a N-depleted phase similar to cubic Mo3N. Other than that, no additional phase formation (like w-AlN) or decomposition could be detected. Contrary to these three coatings — where no w-AlN formation could be detected or any other binary phase (ternary or quaternary fcc-phases could still be hidden behind the major XRD peaks of the parent phase) — the (Al,Cr,Nb,Ta,Ti)N coating (Fig. 5, topmost pattern) exhibits a distinct formation of w-AlN (peak at ≈33 °). Here, also the formation of fcc-AlN seems to be plausible, see the right-hand shoulder of the (220) reflex, indicating a spinodal decomposition process (without nucleation and growth) in this sample, but we cannot draw this conclusion from the other coatings. Other
phases like NbN or TaN, which were predicted to form, cannot be detected due to the sluggish kinetics. The driving force for AlN formation is the highest among the constituents and we still see some fcc-AlN, therefore we can deduce that our annealing process is too mild to finish the decomposition reaction. Thus, the NbN and TaN formation would take an even more severe heat treatment to be initiated or completed. A plausible explanation is also that, the generated strains (due to the formation of w-AlN) lead to the stagnation of the decomposition process [19]. Since this material contains no Mo or W, which are prone to lose N, the observed decomposition behavior matches the predicted one best of the investigated coatings. The results prove that the configurational entropy alone is not sufficient to fully stabilize AlN thermodynamically in an fcc lattice.

To complement the phase evolution with chemical analysis at the nanometer scale, APT was performed for as-deposited and annealed coatings. The results are presented and discussed in sequence of increasing predicted strain stabilization: (Al,Mo,Ta,V,W)N, (Al,Cr,Nb,Ta,Ti)N, (Al,Ti,Mo,V,Zr)N, and (Al,Mo,Ta,V,W)N are shown in Figs. 6, 7, 8, and 9, respectively. The reconstructions of atomic positions, chemical composition profiles as well as frequency distribution analyses with Pearson correlation coefficients close to 0 (Figs. 6 to 9a-c) emphasize the formation of a random solid solution in the as-deposited state for all material systems.

The (Al,Mo,Ta,V,W)N system exhibits the largest driving force for decomposition among the experimentally studied coatings and the massive formation of Al-rich regions upon annealing can be observed by isoconcentration surfaces with ≥ 20 at.% Al (Fig. 6d). The composition profile from the cylindrical region (Fig. 6e, cylinder indicated in d) reveals a chemical modulation with alternations between Al-rich and (Mo,Ta,V,W)-rich regions. The proximitity histogram of regions with ≥ 20 at.% Al (Fig. 6f) demonstrates that the Al content increases from 2 to 34 at.%, while especially Ta and V are reduced. From Ta and V isoconcentration surfaces (Fig. 6d) as well as proximity histograms (not shown) it is evident that these species co-segregate, indicating an early stage of (Ta,V)N segregation which has been observed in decomposed (Mo,Ti,V,Zr)N [6]. Hence, the APT data provide evidence for strong decomposition reactions, governed by Al diffusion for (Al,Mo,Ta,V,W)N.

Also the (Al,Cr,Nb,Ta,Ti)N coating exhibits Al-rich regions after annealing (Fig. 7d), highlighted by ≥ 45 at.% isoconcentration surfaces. The chemical composition profile (Fig. 7e) as well as the proximity histogram (Fig. 7f) reveal the formation of AlN in agreement with the identified wurtzite phase by XRD data (compare Fig. 5b). The apparent reduction of N in the AlN-rich regions is a measurement artifact and can be understood by the electric field strength dependent accuracy of N quantification [60]. Since the required electric field strength for evaporation of Al is significantly lower than for transition metals such a Ti [88], underestimation of N in Al-rich regions is caused by the formation of neutral fragments upon dissociation of molecular ions [89]. Despite the local formation of wurtzite AlN, (Al,Cr,Nb,Ta,Ti)N exhibits a higher thermal stability than the entirely decomposed Al,Mo,Ta,V,W)N coating (compare Fig. 6d-e), which is in very good agreement with our predictions.

The decomposition of (Al,Mo,Ta,V,Zr)N is dominated by Al, Mo, and N as evident from the atomic positions which are shown together with isoconcentration surfaces in Fig. 8d. The chemical composition profile (Fig. 8e) reveals alternations between Al- and Mo-rich regions. Moreover, the surface-near region contains up to 10 at.% O. Hf and O isoconcentration surfaces indicate Hf-O co-segregation which can be rationalized by the high affinity of Hf for oxide formation. The proximity histogram of regions with ≥ 40 at.% Mo in Fig. 8f emphasizes the instability of the Mo-N bond as the Mo content increases locally up to 70 at.% and N is reduced from

### Table 3

Chemical compositions in at.% analyzed with EDS. Standard deviations are ±3 at.% for N, ±2 at.% for W, and ±1 at.% for all other metals.

<table>
<thead>
<tr>
<th>Material</th>
<th>Al</th>
<th>Cr</th>
<th>Mo</th>
<th>Nb</th>
<th>Ta</th>
<th>Ti</th>
<th>V</th>
<th>W</th>
<th>Zr</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Al,Cr,Nb,Ta,Ti)N</td>
<td>8</td>
<td>12</td>
<td>9</td>
<td>15</td>
<td>9</td>
<td>12</td>
<td>10</td>
<td>10</td>
<td>49</td>
<td></td>
</tr>
<tr>
<td>(Al,Mo,Ti,V,Zr)N</td>
<td>8</td>
<td>11</td>
<td>9</td>
<td>15</td>
<td>9</td>
<td>12</td>
<td>10</td>
<td>10</td>
<td>49</td>
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<tr>
<td>(Al,Mo,Ta,V,W)N</td>
<td>8</td>
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<td>(Al,Mo,Ta,V,W)N</td>
<td>8</td>
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</table>

Fig. 5. XRD analysis of the 4 experimentally investigated coatings deposited on sapphire before (a), and after 30 h vacuum-annealing at 800 °C (b). In the as-deposited state all coatings show a single phase fcc structure. After annealing, only (Al,Cr,Nb,Ta,Ti)N shows the formation of w-AlN and possibly fcc-AlN. (Al,Mo,V,Zr)N and (Al,Mo,Ta,V,W)N exhibit N-loss, hence, only (Al,Mo,Ti,V,Zr)N seems to be unaffected by this annealing treatment.
Fig. 6. Local chemical composition analysis of (Al,Mo,Ta,V,W)N in as-deposited and annealed state by atom probe tomography (APT). (a) Reconstruction of Al, Mo, Ta, V, W, and N atomic positions in as-deposited state. (b) Composition profile from the cylindrical region indicated in (a). (c) Frequency distribution analysis with Pearson correlation coefficients which are based on the comparison of the measured distribution with a random, binomial distribution. (d) Reconstruction of Al, Mo, Ta, V, W, and N atomic positions after annealing together with chemically enriched regions represented by isoconcentration surfaces ≥ 20 at.% Al, 20 at.% Mo, 15 at.% Ta, 20 at.% V, and 25 at.% W, as well as ≤ 39 at.% N. (e) The composition profile from the cylindrical region indicated in (d). (f) Proximity histogram of regions with ≥ 20 at.% Al.

Fig. 7. Local chemical composition analysis of (Al,Cr,Nb,Ta,Ti)N in as-deposited and annealed state by APT. (a) Reconstruction of Al, Cr, Nb, Ta, Ti, and N atomic positions in as-deposited state. (b) Composition profile from the cylindrical region indicated in (a). (c) Frequency distribution analysis with Pearson correlation coefficients which are based on the comparison of the measured distribution with a random, binomial distribution. (d) Reconstruction of Al, Cr, Nb, Ta, Ti, and N atomic positions after annealing and Al-rich regions are represented by isoconcentration surfaces with ≥ 45 at.% Al. (e) Composition profile from the cylindrical region indicated in (d). (f) Proximity histogram of regions with ≥ 45 at.% Al.

38 to 10 at.%). While the Mo segregations appear to be more pronounced than Al, it has to be considered that in the as-deposited state the amount of Al is with ∼ 8 at.% significantly lower than Mo with ∼ 13 at.% (concentrations based on EDS analysis).

Finally, the (Al,Hf,Ti,V,Zr)N system exhibits the highest thermal stability as only a few, comparatively small, Al-rich clusters are observed (Fig. 9d), while the distribution of the other constituent elements is very similar to the as-deposited state. Hence, the (Al,Hf,Ti,V,Zr)N coating exhibits the lowest driving force for decomposition among the experimentally studied coatings in agreement with the predicted strain stabilization. However, the chemical composition profile as well as the proximity histogram (Fig. 9e and
Fig. 8. Local chemical composition analysis of (Al,Hf,Mo,V,Zr)N in as-deposited and annealed state by APT. (a) Reconstruction of Al, Hf, Mo, V, Zr, N, and O atomic positions in as-deposited state. (b) Composition profile from the cylindrical region indicated in (a). (c) Frequency distribution analysis with Pearson correlation coefficients which are based on the comparison of the measured distribution with a random, binomial distribution. (d) Reconstruction of Al, Hf, Mo, V, Zr, N, and O atomic positions after annealing together with chemically enriched regions represented by isosurfaces with ≥ 20 at.% Al, 16 at.% Hf, 40 at.% Mo, 25 at.% V, 15 at.% Zr, and 13 at.% O, as well as < 28 at.% N. (e) Composition profile from the cylindrical region indicated in (d). (f) Proximity histogram of regions with ≥ 40 at.% Mo.

Fig. 9. Local chemical composition analysis of (Al,Hf,Ti,V,Zr)N in as-deposited and annealed state by APT. (a) Reconstruction of Al, Hf, Ti, V, Zr, and N atomic positions in as-deposited state. (b) Composition profile from the cylindrical region indicated in (a). (c) Frequency distribution analysis with Pearson correlation coefficients which are based on the comparison of the measured distribution with a random, binomial distribution. (d) Reconstruction of Al, Hf, Ti, V, Zr, and N atomic positions after annealing and Al-rich regions are represented by isosurfaces with ≥ 20 at.% Al. (e) Composition profile from the cylindrical region indicated in (d). (f) Proximity histogram of regions with ≥ 20 at.% Al.
f) show signs of local Al enrichment at the nanometer scale, caused by endothermic mixing, which is also consistent with the predictions. Hence, we show that while the mixing enthalpy drives the decomposition of all the Al-containing HESN studied here, the predicted strain stabilization clearly prevents the formation of w-AlN in (Al, Hf, Ti, V, Zr)N after 30 h vacuum annealing. With insufficient strain stabilization, for example in (Al, Cr, Nb, Ta, Ti)N, decomposition and formation of w-AlN is observed, consistent with our predictions.

3.2.2. Mechanical properties

All coatings investigations show a hardness H between 32 and 36 GPa and an indentation modulus E between 430 and 520 GPa in their as-deposited state (see Supplementary Table 3 for details). The mechanical properties are only slightly influenced by the vacuum annealing treatment for 30 h at 800 °C. Essentially, H and E remain within the error of measurement, with two exceptions: (Al, Hf, Mo, V, Zr)N experiences a reduction in H from ~34 to ~26 GPa, while for (Al, Mo, Ta, V)N the indentation modulus increases from ~514 to ~595 GPa. The increased indentation modulus for the latter could be within the error of measurement, but the hardness reduction for (Al, Hf, Mo, V, Zr)N is statistically significant and can be explained by the more pronounced structural change of this coating (see Fig. 5) involving N-loss, and surface oxidation (see Supplementary Fig. 4). Although the formation of w-AlN could be detected in (Al, Cr, Nb, Ta, Ti)N, its fraction is too small to cause negative impact on the mechanical properties, while the additionally present fcc-AlN is even beneficial in terms of age hardening effects [13].

4. Conclusions

Based on the theoretical and experimental data presented here, it is evident that the impact of the entropy stabilization, often mentioned as major advantage of high-entropy ceramics over lower-entropy counterparts, has been overestimated in the past. For the here studied nitrides, T - S_{config} for reasonable temperatures is still below enthalpy contributions, which are often much larger in ceramics than for metallic alloys.

Caused mostly by the formation of w-AlN, the enthalpic driving forces for decomposition dominate the thermodynamic landscape in the investigated Al-containing nitrides. While ΔH_{mix} ranges from 0.10 to 0.27 eV/atom, the average entropic benefit at 1073 K amounts to only ~0.06 eV/atom, too small to compensate the ΔH_{mix}-governed decomposition driving force. This predicted formation of AlN was confirmed by our XRD and APT investigations. This is also the case for (Al, Hf, Ti, V, Zr)N, but the Al-enriched regions are much smaller in this sample compared to the other materials. Future attempts at finding thermodynamically stable ceramic compounds, without taking enthalpic interactions between the elements into account, are thus incomplete.

In the case of Al-containing nitrides, the strain stabilization, caused by the larger volumes of the thermodynamically stable binary phases, can have a much larger impact (~0.01 to ~0.28 eV/atom) on the decomposition behavior than T - S_{config}. Among the investigated compositions, 22 were predicted to be strain stabilized against decomposition and good agreement between predictions and experimental data was obtained for (Al, Hf, Ti, V, Zr)N, where a positive mixing enthalpy drives the decomposition, but the reaction is hindered by strain, resulting in almost no elemental segregation. Hence, it is reasonable to assume that this principle of strain stabilization can also be applied to other material classes. While considering enthalpy changes [79], screening for large volume mismatches between materials and their expected decomposition products can provide an efficient path to potentially strain stabilized compositions.

The expectations should also be adjusted for the lattice distortion, another core-effect of high-entropy materials. Our analysis of the radial distribution function shows that a large number of alloyed elements alone does not guarantee a highly distorted lattice. While more elements increase the probability of resulting in a moderate to large lattice distortion, the system (HfMoNbTaW)N for example is predicted to result in a lower lattice distortion than commonly observed for many ternary or quaternary compounds. Clearly, the size mismatch has to be tailored to maximize the lattice distortions.

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 material


References


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