First Principles Modeling and Simulation of Zr-Si-B-C-N ceramics: Developing Hard and Oxidation Resistant Coatings

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Abstract:

We model amorphous ZrSiBCN ceramics combining ab-initio molecular dynamic simulations with melt-quench and simulated annealing techniques. Starting from the parent composition $\text{Zr}_{42}\text{B}_{32}\text{C}_8\text{N}_{18}$ we systematically increase the Si_3N_4 content along four different pathways in the composition diagram and evaluate trends in structure and properties. Mixtures of ZrB_2 , ZrN , and ZrC exhibit Zr layers as well as ZrB_2 and ZrN(C) nuclei, but addition of Si_3N_4 reduces structural order in the models. Elastic moduli decrease with increasing Si_3N_4 content to values less than expected of a simple mixture model. Thus, while addition of Si_3N_4 to amorphous ZrBCN coatings may improve oxidation resistance, this needs to be balanced with desired mechanical properties.

Keywords:

Hard coatings, density functional theory calculations, ab-initio molecular dynamics, elastic moduli, nucleation

Introduction:

Zirconium borides, carbides and nitrides are ultra high temperature ceramics (UHTCs) with melting points above 3000 °C. [1, 2] They are frequently used as protective coatings due to their refractory nature and high hardness. [3, 4] Thin films of ZrB₂, ZrC, or ZrN are synthesized via physical vapor deposition (PVD) processes, for instance by reactive magnetron sputtering [5] or via chemical vapor deposition (CVD) techniques. [6, 7] In a recent study, quaternary ZrBCN films with thickness between 3.5 and 4.1 μm have been synthesized by pulsed magnetron sputtering of Zr and B₄C targets in flowing N₂. [8, 9] These coatings exhibit hardness up to 36 GPa, and the high value is attributed to a nano-domain structure of ZrN grains joined via monolayer interfaces. [8, 9]

At elevated temperatures zirconium-based UHTCs have poor oxidation resistance, unfortunately. [10] ZrB₂ forms ZrO₂ and B₂O₃ upon oxidation, and although a protective layer of glassy B₂O₃ forms, it evaporates rapidly at temperatures exceeding 1200 °C exposing a non-protective ZrO₂ layer. [11-13] Zirconium carbides oxidize at temperatures lower than ZrB₂, at 1000 °C. [14] Zirconium nitrides have the least oxidation resistance forming ZrO₂ at temperatures as low as 500 °C. [15-17] The quaternary ZrBCN films mentioned above show strong oxidation at 800 °C. [8, 9]

An approach to improve oxidation resistance of zirconium borides at high temperatures is the addition of a silicon bearing compound, for example silicon nitride [18] or silicon carbide. [19] Significant improvements to oxidation resistance (up to 1900 °C) have been reported for ZrB₂ and 20 vol% SiC composites. [20][21][22] Oxidation resistance of ZrB₂-Si₃N₄ ceramics was found to increase to 1300-1400 °C with increasing Si₃N₄ content due to formation of a protective layer of borosilicate glass. Addition of 10 mol% of Cr and Ta diborides to these ZrB₂-Si₃N₄ coatings improved the oxidation resistance further. [23]

The high temperature mechanical properties of these materials have also been another prominent field of study. Addition of 20 vol% SiC to ZrB₂ decreases the Young's modulus of 510 GPa at room temperature to 420 GPa at 1400 °C.[24] At 1600 °C, the Young's modulus then plunges to 100 GPa. Another study finds the Young's modulus of ZrB₂-SiC composites dropping to 210 GPa at 1500 °C compared to 510 GPa at room temperature.[25] This decrease in Young's modulus is attributed to the presence of oxides at grain boundaries in the polycrystalline material. [26] The presence of 5% Si₃N₄ as a sintering aid in pure ZrB₂ also lowers the Young's Modulus to 419 GPa.[27] At room temperature, ZrB₂-SiC composites have exhibited Vickers hardness of 17-24 GPa depending on the SiC particle size.[28, 29] Addition of Si₃N₄ to ZrB₂ and SiC (ZrB₂+20 SiC+4 Si₃N₄), decreases hardness to ~14 GPa.[27]

In this work, we will investigate the impact of Si₃N₄ addition on structure and properties of ZrSiBCN materials using structure modeling and ab-initio calculations. Previously, Houska et al. used computational methods to investigate atomic and electronic structure of ZrBCN.[30] They compared different compositions and characterized covalent and metallic bonding in these materials. They used rock-salt type Zr(N+C+B) solid-solutions as models to rationalize the high hardness observed in ZrBCN films. The same group also studied some MSiBCN (M = Ti, Hf and Zr) films and investigated the impact of the metal M on segregation and oxidation resistance.[31]

Our exploration starts with the composition Zr₄₂B₃₂C₈N₁₈, a ternary mixture of ZrN, ZrB₂, and ZrC. This composition is close to the composition Zr₄₁B₃₀C₈N₁₉ of sputtered films, for which a hardness of 36 GPa has been measured.[8, 9] Varying the ZrN, ZrB₂, and Si₃N₄ phase content, we generate structure models via melt-quench and subsequent annealing techniques. We will show that formation of nm-sized ZrN and ZrB₂ nuclei happens even at the short time-scales of our computer simulation. We compute elastic moduli and Vickers hardness and highlight the impact of Si₃N₄ addition to ZrSiBCN materials.

Computational details:

Structures and energies of ZrSiBCN models and of crystalline reference phases are computed within density functional theory (DFT). [32-36] We use the Generalized Gradient Approximation (GGA) [37], [38] for electron exchange and correlation together with the Projector Augmented Wave (PAW) method. [39, 40] For optimizations and property calculations we use a cut-off of 350 eV for the expansion of the wave function into a plane wave basis set. Sampling of the Brillouin zone is done at the Γ -point for amorphous models and using appropriate meshes for all crystalline models.

We create structures of amorphous ZrSiBCN by a “melt-quench” approach, which is followed – for selected models – by a sequence of simulated annealing. For both melt-quench and the simulated annealing processes, we perform ab-initio molecular dynamic (aiMD) simulations under a canonical (NVT) ensemble. We use a time-step of 2 fs for integrating the equations of motion and control temperature via velocity rescaling. The velocity rescaling is performed at every time-step. To save computational costs, we reduce the cutoff energy to 205 eV during aiMD simulations. In the beginning of the melt-quench procedure, we place 100 atoms randomly into a box with a volume approximately reflecting a mixture of the constituting phases ZrB₂, ZrN, ZrC, and Si₃N₄. For example, models with composition Zr₄₂B₃₂C₈N₁₈ are initially set to a density of 6.0 g/cm³, and adding Si₃N₄ lowers the density accordingly. Then we create a “liquid” state via simulation at 5000 K for 10 ps (5,000 time-steps) during which the system loses all memory of its initial configuration. This randomization is supported by the fact that atoms exchange more than 90% of their nearest neighbors during this period.

Subsequently, the ensemble is cooled to 3000 K within 20 ps, which corresponds to a cooling rate of 10^{14} Ks⁻¹. At 3000 K, the system is again equilibrated for 20 ps, after which it is cooled to 2000 K within 20 ps (cooling rate of $5 \cdot 10^{13}$ Ks⁻¹) and finally down to 300 K in 20 ps (cooling rate of $8.5 \cdot 10^{13}$ Ks⁻¹). The overall simulation time to generate a

“melt-quench” structure in this study is almost two orders of magnitude (about 50 times) longer than in Ref. [30]. The time-temperature sequence of the melt-quench process is displayed in Figure 1 (left). For each composition, we generate five independent models via the melt-quench procedure (total 65 models). All structures obtained after the melt-quench procedure are finally optimized (positions and cell parameters) by converging forces to 5 meV/Å and stresses below 1 kBar. Final volumes of optimized models are within 3% of their initial volume.

Simulated annealing starts after optimization of melt-quench models. For every composition, we choose the melt-quench model with lowest energy and simulate this at 800 K for 2 ps (total 13 models). Then we sequentially heat the model to 1200, 1800, 2200, 2600, 3000, and 3400 K using a heating rate of $2.5 \times 10^{14} \text{ K s}^{-1}$, while keeping the temperature constant for 5 to 20 ps once the desired temperature has been achieved. A graph with the temperature profile during simulated annealing is shown in Figure 1 (right). During the annealing procedure, we take a snapshot of the model every 2 ps and optimize the structure, while the annealing simulation continues. The optimized configuration tracks the underlying potential energy surface, above which the structure evolves at elevated temperatures. Moreover, since the annealing procedure effectively “heals” structural defects, we receive a sequence of models of which some have energies lower than the initial configurations. After a first complete annealing simulation, we choose the lowest energy model once again and repeat the annealing procedure all over. This is illustrated in Figure 2 for the model of $\text{Zr}_{27}\text{Si}_{15}\text{B}_{22}\text{C}_8\text{N}_{28}$. The figure on the left illustrates the first annealing process. The red dot shows the energy of the initial structure of this model of $\text{Zr}_{27}\text{Si}_{15}\text{B}_{22}\text{C}_8\text{N}_{28}$ as received after optimization of the melt quench model. Some healing of structural imperfections occurs during annealing at 1800 K, and a new “lowest energy structure” for the model is found. Further annealing during this run does not produce a lower energy structure, so the model is taken and, once again, subjected to a second annealing procedure. During the second annealing procedure, for

which longer “holding” times have been chosen (see Fig. 2 (right)), another drop in energy is observed. A third annealing process (not shown here) did not produce a model with even lower energy. In general, we consider a model being “converged” with respect to energy gains, if the maximum gain within annealing was less than 1 eV for 100 atoms (0.01 eV/atom).

We compute elastic constants c_{ij} via the strain-stress relationship given by Hooke’s Law for all models, those received after the melt-quench procedure (5 for each composition) and for models with lowest energy obtained from the annealing procedure (1 for each composition). Details of the computational procedure have been given in Ref.[41]. We estimate Bulk modulus (B), Young’s modulus (E), and shear modulus (G) as well as Poisson’s ratio for each structure within the approximations of Voigt, Reuss and Hill.[42-44] We evaluate Vickers Hardness, H_v , using its empirical relation to B and G as proposed by Chen et al..[45]

Results:

a) Composition Diagram

We investigate ZrSiBCN structures with composition located in the quaternary ZrB₂-ZrN-ZrC-Si₃N₄ phase diagram. Every model comprises of 100 atoms. We compute mole coefficient and mole fraction (mol%) directly from composition, e.g. $Zr_{25}Si_{18}B_{16}C_8N_{33} == 8 \cdot ZrC + 9 \cdot ZrN + 8 \cdot ZrB_2 + 6 \cdot Si_3N_4 == 25.8 \text{ mol\% ZrC} + 29.0 \text{ mol\% ZrN} + 25.8 \text{ mol\% ZrB}_2 + 19.4 \text{ mol\% Si}_3\text{N}_4$. We fix the amount of ZrC in all models (8 formula units of ZrC) and represent the composition of the remaining ZrB₂-ZrN-Si₃N₄ content in a ternary diagram (Figure 3). We acknowledge that this is not a perfect slice of the quaternary phase diagram, since the mol% of ZrC in the ZrSiBCN structures varies depending on the content of the other constituents. The small amount of ZrC is very helpful for structure

simulations, because C may substitute for both N (in ZrN-like arrangements) and B (in ZrB₂-like fragments).

Starting from the “parent” composition of Zr₄₂B₃₂C₈N₁₈ (Zr₄₂B₃₂C₈N₁₈ = 8·ZrC + 18·ZrN + 16·ZrB₂), which is close to the experimentally realized composition of Zr₄₁B₃₀C₈N₁₉— we adopt four different pathways (1)-(4) to incorporate Si₃N₄. These paths are indicated in the ternary composition diagram shown in Figure 3. Along each pathway we add units of Si₃N₄ to the model, while balancing the total number of atoms in a model (100) by changing the amount of ZrB₂ and ZrN. The net change along the four pathways is (1) + Si₃N₄ – ZrB₂ – 2 ZrN, (2) + 6 Si₃N₄ – 8 ZrB₂ – 9 ZrN, (3) + 2 Si₃N₄ – 4 ZrB₂ – ZrN, and (4) + Si₃N₄ – 3 ZrB₂ + ZrN. Path (1) is almost parallel to the ZrN-Si₃N₄ tie-line, while path (3) is approximately parallel to the ZrB₂-Si₃N₄ tie-line.

We generate five independent models for each composition via the melt-quench procedure, and subject the lowest-energy model of each composition to the simulated annealing procedure. From the annealing procedure we receive one more model for each composition. Hence, in total we analyze six models for each of the 13 compositions. For reference, we compute crystalline structures of ZrB₂, ZrC and ZrN (both NaCl-type), β-Si₃N₄, h-BN and c-BN.

b) Structure and Ordering:

Figure 4 shows four representative structures from each of the four pathways as obtained after two cycles of simulated annealing. It is difficult to provide simple quantitative measures for bonding in these mixed systems. However, we find average bond distances comparable with those computed for crystal structures. For instance, Zr-B (2.42 Å in the model; 2.54 Å in hexagonal ZrB₂), Zr-C (2.34 Å; 2.34 Å in c-ZrC), Zr-N (2.37 Å; 2.31 Å in c-ZrN), Si-N (1.77 Å; 1.75 Å in β-Si₃N₄), Si-C (1.81 Å; 1.86 Å in β-SiC), B-B (1.72 Å; 1.83 Å in hexagonal ZrB₂), and B-N (1.47 Å; 1.45 Å in h-BN). C-C, C-N, and N-N bonds do not

appear in these models. We also find occasionally some Zr-Si bonds (2.79 Å; 2.72 Å in ZrSi₂).

Simulated site-site distance pair correlation functions $g(r)$ of two models – Zr₃₉Si₃B₃₀C₈N₂₀ (pathway (1) at 3 mol% Si₃N₄) and Zr₂₅Si₁₈B₁₆C₈N₃₃ (pathway (2) at 19 mol% Si₃N₄) shown in Figure 5 support our observations. In particular, partial $g(r)$'s show that both systems exhibit no C-C, C-N, or N-N bonding. Zr...Zr correlations at 3.2-3.3 Å are comparable to distances between Zr layers in hexagonal ZrB₂ (3.17 Å), c-ZrN (3.27 Å) and c-ZrC (3.30 Å).

We can characterize – qualitatively – the structural order that occurs in these Zr-Si-B-C-N models. Zr tends to arrange in layers, each layer resembling closest packing (cp) in a plane. Interstitial spaces between the layers are filled with N, C and B in such a way that Zr is, ideally, six-fold coordinated. These Zr-centered octahedra fuse together and form small nuclei of ZrN(C) (Figure 6, left). B atoms tend to aggregate in B-B networks forming rings like in the honeycomb B-substructure of ZrB₂, with Zr located above and below the rings (Figure 6, right). The ZrB₂ nuclei do not appear as frequent as ZrN(C) nuclei. These fragments and nuclei appear in melt-quench models and annealed models alike, with more pronounced order in the latter.

The impact of increasing Si₃N₄ content is a decreasing tendency to form nuclei of any kind. For example, models with two and more units of Si₃N₄ are free of B₆-rings. Moreover, the number of Zr-centered octahedra fused together (size of ZrN(C) nuclei) decreases significantly as the Si₃N₄ content increases. Overall, structures containing Si₃N₄ are less ordered and exhibit a larger variety of local environments for all atoms.

c) Thermochemistry:

In Table 1 we show the computed enthalpy of formation of ZrSiBCN models. For each composition we only consider the model with the lowest energy. The enthalpy of

formation is defined with reference to the crystal structures ZrN, ZrC, ZrB₂, and β -Si₃N₄, according to:

$$\Delta H_f = E(a\text{-ZrSiBCN}) - [m \cdot E(c\text{-ZrB}_2) + n \cdot E(c\text{-ZrN}) + p \cdot E(c\text{-ZrC}) + r \cdot E(\beta\text{-Si}_3\text{N}_4)] / n_{\text{atoms}}$$

where m,n,p and r stand for formula units(f.u.) of c-ZrB₂, c-ZrN, c-ZrC and β -Si₃N₄ respectively. Reference energies for the crystalline structures are:

c-ZrB₂ = -24.74 eV/f.u.; c-ZrC = -19.33 eV/f.u.; c-ZrN = -20.23 eV/f.u.; β -Si₃N₄ = -58.69 eV/f.u.

Overall, ΔH_f of these models is about 0.4-0.5 eV/atom with the exception of the parent model, Zr₄₂B₃₂C₈N₁₈, for which the enthalpy of formation is only half as high, 0.24 eV/atom. For amorphous Si₃N₄ itself, we find consistently a value of 0.2 – 0.3 eV/atom for the enthalpy of formation, which parallels earlier investigations.[46] Hence, the addition of Si₃N₄ to a phase assemblage of ZrB₂, ZrC, and ZrN significantly increases ΔH_f . This increase of ΔH_f parallels the observed decrease to form ordered nuclei with addition of Si₃N₄.

Pathway	Composition	Energy (eV/atom)	m	n	p	r	ΔH_f (eV/atom)
Parent	Zr ₄₂ B ₃₂ C ₈ N ₁₈	-9.81	16	18	8	0	0.24
Pathway (1)	Zr ₃₉ Si ₃ B ₃₀ C ₈ N ₂₀	-8.67	15	16	8	1	0.41
	Zr ₃₆ Si ₆ B ₂₈ C ₈ N ₂₂	-8.57	14	14	8	2	0.45
	Zr ₃₃ Si ₉ B ₂₆ C ₈ N ₂₄	-8.49	13	12	8	3	0.46
	Zr ₃₀ Si ₁₂ B ₂₄ C ₈ N ₂₆	-8.40	12	10	8	4	0.48

	$\text{Zr}_{27}\text{Si}_{15}\text{B}_{22}\text{C}_8\text{N}_{28}$	-8.31	11	8	8	5	0.51
Pathway (2)	$\text{Zr}_{25}\text{Si}_{18}\text{B}_{16}\text{C}_8\text{N}_{33}$	-8.35	8	9	8	6	0.52
Pathway (3)	$\text{Zr}_{37}\text{Si}_6\text{B}_{24}\text{C}_8\text{N}_{25}$	-8.68	12	17	8	2	0.45
	$\text{Zr}_{32}\text{Si}_{12}\text{B}_{16}\text{C}_8\text{N}_{32}$	-8.63	8	16	8	4	0.48
	$\text{Zr}_{27}\text{Si}_{18}\text{B}_8\text{C}_8\text{N}_{39}$	-8.64	4	15	8	6	0.45
Pathway (4)	$\text{Zr}_{40}\text{Si}_3\text{B}_{26}\text{C}_8\text{N}_{23}$	-8.77	13	19	8	1	0.43
	$\text{Zr}_{38}\text{Si}_6\text{B}_{20}\text{C}_8\text{N}_{28}$	-8.86	10	20	8	2	0.38
	$\text{Zr}_{36}\text{Si}_9\text{B}_{14}\text{C}_8\text{N}_{33}$	-8.87	7	21	8	3	0.42
	$\text{Zr}_{34}\text{Si}_{12}\text{B}_8\text{C}_8\text{N}_{38}$	-8.91	4	22	8	4	0.43

Table 1: Enthalpy of formation(ΔH_f) of α -ZrSiBCN with respect to crystalline phases(ZrB_2 , ZrN , ZrC and β - Si_3N_4). For each composition only the model with lowest energy was considered. Columns m, n, p, and r show formula units (f.u.) of α - ZrB_2 , α - ZrN , α - ZrC and β - Si_3N_4 , respectively.

d) Elastic Moduli and Vickers hardness:

Elastic constants c_{ij} (there are 21 independent elements of c_{ij} for each model, since the structures do not possess any symmetry) are computed for all ZrSiBCN models, six for each composition. The stiffness matrix (c_{ij}) of an isotropic model comprises two independent values only, since $c_{11} = c_{22} = c_{33}$, $c_{12} = c_{23} = c_{13}$ and $c_{44} = c_{55} = c_{66} = (c_{11} - c_{12})/2$. All other elements vanish.[47] This is not fulfilled for individual models we constructed, most likely because their size is not large enough to be “isotropic”.

However, averaging c_{ij} for models of the same composition yields isotropic behavior within the margin of error. A representative average stiffness matrix, for composition $Zr_{39}Si_3B_{30}C_8N_{20}$, is shown in Table 2:

c_{ij}	1	2	3	4	5	6
1	266 ± 14	137 ± 9	118 ± 5	-20 ± 17	13 ± 13	5 ± 6
2	137 ± 9	258 ± 7	114 ± 9	10 ± 11	-17 ± 7	-7 ± 5
3	118 ± 5	114 ± 9	265 ± 15	-11 ± 9	12 ± 9	6 ± 3
4	-20 ± 17	10 ± 11	-11 ± 9	61 ± 16	19 ± 14	4 ± 5
5	13 ± 13	-17 ± 7	12 ± 9	19 ± 14	58 ± 10	0 ± 6
6	5 ± 6	-7 ± 5	6 ± 3	4 ± 5	0 ± 6	82 ± 4

Table2: Stiffness matrix [6x6] of $Zr_{39}Si_3B_{30}C_8N_{20}$ averaged over 5 independent melt-quench models. For each entry of c_{ij} we list the value together with the standard error. The minimum and maximum standard errors are 3 and 16 GPa, respectively, with an average of 9 GPa.

Using the stiffness (c_{ij}) and compliance (s_{ij}) matrices, we compute the elastic moduli B, G and E using the Voigt, Reuss and Hill (V-R-H) approach.[42-44] Voigt's method yields an upper boundary for an elastic modulus: bulk modulus $B_V = (1/9)[(c_{11} + c_{22} + c_{33}) + 2(c_{12} + c_{13} + c_{23})]$ and shear modulus $G_V = (1/15)[(c_{11} + c_{22} + c_{33}) - (c_{12} + c_{13} + c_{23}) + 3(c_{44} + c_{55} + c_{66})]$. Reuss's method provides a lower bound of an elastic modulus: $B_R = [(s_{11} + s_{22} + s_{33}) + 2(s_{12} + s_{13} + s_{23})]^{-1}$ and $G_R = 15 [4(s_{11} + s_{22} + s_{33}) - (s_{12} + s_{13} + s_{23}) + 3(s_{44} + s_{55} + s_{66})]^{-1}$. The Hill method gives an average of the upper and lower bounds as $B_H = (1/2)(B_V + B_R)$ and $G_H = (1/2)(G_V + G_R)$. The Young's modulus (E) is related to the bulk

(B) and shear (G) moduli as $E = 9BG/(3B+G)$, and our estimate of E is based on the aggregate Hill values of B and G. For a given composition the moduli can be determined either by first averaging the c_{ij} and computing moduli from the averaged stiffness matrix or alternatively by first computing moduli for each model and then averaging the moduli for each composition. We choose the latter approach, since it provides us a simple error estimate of each modulus based on its average and its variation (in comparison to the requirement to do a full error propagation from stiffness coefficients). Vickers hardness (H_V) is estimated using the empirical relation between hardness and elastic moduli as proposed by Chen: $H_V = 2 (G^3/B^2)^{0.585} - 3$. [45]

In Table 3, we summarize results of elastic moduli and hardness (H_V) for crystalline structures, the parent composition $Zr_{42}B_{32}C_8N_{18}$ and for ZrSiBCN models. There is reasonable agreement between our computed data with references in literature. For example, experimental data for the independent elastic constants of hexagonal ZrB_2 (space group: P6/mmm) are $c_{11}=581$ GPa, $c_{12}=55$ GPa, $c_{13}=121$ GPa, $c_{33}=445$ GPa, and $c_{44}=240$ GPa. [48] This yields B, G, E of 244 GPa, 233 GPa, and 530 GPa, respectively, within the V-R-H approximation. Our computed moduli for ZrB_2 are 247 GPa, 214 GPa, and 499 GPa, for B, G, and E, respectively, with a deviation of less than 10% from the experimental data. For crystalline ZrC , we compute moduli B and G to 236 GPa and 146 GPa, respectively, which provides an estimate of 18 GPa for H_V . This is in close agreement with recent computational data (B = 234 GPa, G = 164 GPa, $H_V = 23$ GPa, [49]), and differences arise only from the use of different pseudopotentials and cut-offs ($E_{cut-off} = 350$ eV against 560 eV in reference [49]). Experimental values of B for ZrC , which depend on the measurement technique and sample microstructure, range between 207 and 223 GPa. [50], [51] Our computed elastic moduli of ZrN are B = 268 GPa, G = 195 GPa, and E = 470 GPa, somewhat larger than recent computational data (B = 245 GPa, G = 150 GPa, E = 375 GPa) [52]. From nano-indentation measurements, the elastic constants for β - Si_3N_4 are determined to be: $c_{11} = 343$ GPa, $c_{12} = 136$ GPa, $c_{13} = 120$ GPa, $c_{33} =$

600 GPa and $c_{44}=124$ GPa. [53] Accordingly, the elastic moduli from V-R-H approximations are $B = 227$ GPa, $G = 120$ GPa, $E = 307$ GPa and $H_V = 13$ GPa. Computational data in reference [54] for β - Si_3N_4 yields values of $B = 225$ GPa and $G = 120$ GPa. [54] Comparison of these values with our computed values listed in Table 3 for β - Si_3N_4 ($B = 236$ GPa, $G = 126$ GPa, $E = 313$ GPa) shows good agreement. [54] For the parent composition $\text{Zr}_{42}\text{B}_{32}\text{C}_8\text{N}_{18}$, we compute B , G , E , and H_V of 171, 79, 206, and 8 GPa, respectively.

In Figure 7 we plot bulk modulus B , shear modulus G , Young's modulus E and Vickers hardness H_V as a function of Si_3N_4 content (mol-% of Si_3N_4) along the selected pathways of the composition diagram (see Fig. 3).

Linear fits to the data in Figure 7 show a decrease of elastic moduli and hardness with increasing Si_3N_4 -content. For instance, addition of 1 mol-% of Si_3N_4 to compositions along pathway(1), decreases the bulk modulus by 1.8 GPa. For pathway(3) and (4) the decrease in B is 1.0 GPa and 2.0 GPa per mol% Si_3N_4 added, respectively. For shear modulus (G) the decrease per mol-% Si_3N_4 is 1.2 GPa for pathway(1), 0.6 GPa for pathway(3) and 1.5 GPa for pathway(4). The decrease in Young's modulus (E) is ~ 3.0 , 1.6 and 4.0 GPa along pathway (1), (3) and (4) respectively. However, Vickers hardness (H_V) drops only slightly (by ~ 0.2 GPa per mol-% Si_3N_4) along each pathway, since the estimate by Chen strongly correlates H_V to the ratio of B and G . Overall, starting from the initial composition $\text{Zr}_{42}\text{B}_{32}\text{C}_8\text{N}_{18}$, an increase of Si_3N_4 content in the ZrSiBCN models results in a decrease of elastic moduli B and G and, ultimately, of Vickers hardness. A decrease in G , E , and H_V (but not in B) can be expected from a simple mixture model applied to the addition of Si_3N_4 to a phase assemblage of ZrB_2 , ZrC , and ZrN . However, we show in next paragraph that effect is larger than expected and that the moduli are impacted additionally by the reduced structural order (as discussed in the previous section).

Along pathway (1) a simple mixture model of $\text{Zr}_{42}\text{B}_{32}\text{C}_8\text{N}_{18}$ based on mole fractions of crystalline ZrN , ZrC and ZrB_2 and moduli of crystalline structures given in Table 3 predicts moduli of 254 GPa, 193 GPa, and 461 GPa, for B, G, and E, respectively. Computed values are 171, 79, and 208 GPa, for B, G, and E, respectively. For the model with largest Si_3N_4 content, $\text{Zr}_{27}\text{Si}_{15}\text{B}_{22}\text{C}_8\text{N}_{28}$, a mixture model yields 198, 102, and 343 GPa, and the computation gives 143, 60, and 159 GPa, for B, G, and E, respectively. Thus, computed models have significantly lower moduli than expected by a mixture model. If data of amorphous $\alpha\text{-Si}_3\text{N}_4$ (either from computed models, or using reported experimental data of $B = 196$ GPa [46] and $E = 289$ GPa [55]) is used to predict the “ideal” moduli for these compositions, the discrepancy is still significant. More importantly, the deviation from an ideal mixture model increases with Si_3N_4 content along all pathways. We note that along pathway (1), (2) and (3) addition of Si_3N_4 happens at the expense of ZrN , while the ZrB_2 content remains almost constant. On the other hand, along pathway (4) Si_3N_4 is added at the expense of ZrB_2 , and the ZrN content increases slightly. Along both paths we observe significant decrease of local order with increase of Si_3N_4 content. Therefore, for these ZrSiBCN models a decrease of elastic moduli correlates with a decrease in structural order, which in turn goes along with an increase of Si_3N_4 content.

	Composition	Bulk Modulus (GPa)	Shear Modulus (GPa)	Young's Modulus (GPa)	Vickers Hardness (GPa)
Crystalline phases	c- ZrB_2	247	214	499	36
	c- ZrN	268	195	470	27
	c- ZrC	236	146	364	18

	$\beta\text{-Si}_3\text{N}_4$	236	126	313	13
Parent	$\text{Zr}_{42}\text{B}_{32}\text{C}_8\text{N}_{18}$	171 ± 8	79 ± 5	206 ± 13	8 ± 4
Pathway (1)	$\text{Zr}_{39}\text{Si}_3\text{B}_{30}\text{C}_8\text{N}_{20}$	190 ± 22	86 ± 4	225 ± 11	8 ± 1
	$\text{Zr}_{36}\text{Si}_6\text{B}_{28}\text{C}_8\text{N}_{22}$	158 ± 4	67 ± 4	177 ± 9	6 ± 1
	$\text{Zr}_{33}\text{Si}_9\text{B}_{26}\text{C}_8\text{N}_{24}$	153 ± 5	71 ± 2	184 ± 5	7 ± 0
	$\text{Zr}_{30}\text{Si}_{12}\text{B}_{24}\text{C}_8\text{N}_2$	152 ± 3	68 ± 1	178 ± 3	6 ± 0
	$\text{Zr}_{27}\text{Si}_{15}\text{B}_{22}\text{C}_8\text{N}_2$	143 ± 3	60 ± 2	159 ± 5	5 ± 0
Pathway (2)	$\text{Zr}_{25}\text{Si}_{18}\text{B}_{16}\text{C}_8\text{N}_3$ 3	144 ± 4	59 ± 3	157 ± 8	5 ± 1
Pathway (3)	$\text{Zr}_{37}\text{Si}_6\text{B}_{24}\text{C}_8\text{N}_{25}$	162 ± 1	73 ± 1	192 ± 3	7 ± 0
	$\text{Zr}_{32}\text{Si}_{12}\text{B}_{16}\text{C}_8\text{N}_3$	157 ± 2	66 ± 3	174 ± 7	5 ± 1
	$\text{Zr}_{27}\text{Si}_{18}\text{B}_8\text{C}_8\text{N}_{39}$	151 ± 3	69 ± 1	179 ± 3	6 ± 0
Pathway (4)	$\text{Zr}_{40}\text{Si}_3\text{B}_{26}\text{C}_8\text{N}_{23}$	168 ± 2	76 ± 4	198 ± 9	6 ± 1
	$\text{Zr}_{38}\text{Si}_6\text{B}_{20}\text{C}_8\text{N}_{28}$	164 ± 1	70 ± 2	184 ± 4	6 ± 0
	$\text{Zr}_{36}\text{Si}_9\text{B}_{14}\text{C}_8\text{N}_{33}$	153 ± 8	59 ± 6	156 ± 15	4 ± 1
	$\text{Zr}_{34}\text{Si}_{12}\text{B}_8\text{C}_8\text{N}_{38}$	151 ± 5	67 ± 2	175 ± 4	6 ± 0

Table 3: Computed B, G, and E and Vickers Hardness of crystalline ZrB_2 , ZrC , ZrN , and Si_3N_4 and of amorphous ZrSiBCN models. For amorphous models the error given refers to the standard error obtained from averaging moduli of individual models.

Conclusion

In this work, we model amorphous ZrSiBCN ceramics, which are candidates for high temperature coating materials. Using melt-quench and simulated annealing techniques

together with ab-initio molecular dynamic simulations, we generate mixtures of ZrB_2 , ZrN , ZrC and Si_3N_4 each model comprising 100 atoms. Starting from the parent composition $\text{Zr}_{42}\text{B}_{32}\text{C}_8\text{N}_{18}$ we follow four different pathways along which Si_3N_4 can be included. Models we receive exhibit Zr layers as well as ZrB_2 and $\text{ZrN}(\text{C})$ nuclei. We observe, qualitatively, that structural order depends on the amount of Si_3N_4 content in the system: the more Si_3N_4 the lower the order. Thermochemical calculations yield an enthalpy of formation (ΔH_f) of $= 0.4\text{--}0.5$ eV/atom for the ZrSiBCN models. We compute independent elastic constants and from those elastic moduli (B, G and E) within the V-R-H approximations. Along each pathway, we observe decrease of B, G, E and H_V with increasing Si_3N_4 content. Values for B, G, E and H_V are lower than expectations from a simple mixture model, indicating additional impact of reduced structural order upon Si_3N_4 addition.

Consequently, while addition of Si_3N_4 to amorphous ZrBCN coating materials may improve the materials' oxidation resistance, the computations show that Si_3N_4 also impacts mechanic performance of the coatings. Most notably, we show that a significant effect arises via reduction in structural order. While sputtered ZrBCN coatings show nano-domain structure with substantial proportion of nano-grains, we expect that addition of Si_3N_4 impedes the formation of nuclei and nano-grains and increases disorder in the films. Thus, the engineers' choice will be a balance between desired oxidation resistance and target mechanical properties.

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Simulated site to site distance pair correlation function

Simulated site to site distance pair correlation function

Pathway (1)

Pathway (3)

Pathway (4)

Pathway (1)

Pathway (3)

Pathway (4)

Pathway (1)

Pathway (3)

Pathway (4)

Pathway (1)

Pathway (3)

Pathway (4)