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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 $Zr_{42}B_{32}C_8N_{18}$ 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.

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1. 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 ZrB_2 , 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 B_4C targets in flowing N_2 [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 UHTC's have poor oxidation resistance, unfortunately [10]. ZrB_2 forms ZrO_2 and B_2O_3 upon oxidation, and although a protective layer of glassy B_2O_3 forms, it evaporates rapidly at temperatures exceeding 1200 °C exposing a non-protective ZrO_2 layer [11–13]. Zirconium carbides oxidize at temperatures lower than ZrB_2 , at 1000 °C [14]. Zirconium nitrides have the least oxidation resistance forming ZrO_2 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 ZrB_2 and 20 vol% SiC composites [20]. [21] [22] Oxidation resistance of ZrB_2 - Si_3N_4 ceramics was found to increase to 1300–1400 °C with increasing Si_3N_4 content due to formation of a protective layer of borosilicate glass. Addition of 10 mol % of Cr and Ta diborides to these ZrB_2 - Si_3N_4 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 ZrB_2 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 ZrB_2 -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% Si_3N_4 as a sintering aid in pure ZrB_2 also lowers the Young's Modulus to 419 GPa [27]. At room temperature, ZrB_2 -SiC composites have exhibited Vickers hardness of 17–24 GPa depending on the SiC particle size [28,29]. Addition of Si_3N_4 to ZrB_2 and SiC

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($\text{ZrB}_2 + 20 \text{ SiC} + 4 \text{ Si}_3\text{N}_4$), decreases hardness to ~ 14 GPa [27].

In this work, we will investigate the impact of Si_3N_4 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 $\text{Zr}(\text{N} + \text{C} + \text{B})$ solid-solutions as models to rationalize the high hardness observed in ZrBCN films. The same group also studied some MSiBCN ($\text{M} = \text{Ti}, \text{Hf}$ and Zr) films and investigated the impact of the metal M on segregation and oxidation resistance [31].

Our exploration starts with the composition $\text{Zr}_{42}\text{B}_{32}\text{C}_8\text{N}_{18}$, a ternary mixture of ZrN, ZrB_2 , and ZrC. This composition is close to the composition $\text{Zr}_{41}\text{B}_{30}\text{C}_8\text{N}_{19}$ of sputtered films, for which a hardness of 36 GPa has been measured [8,9]. Varying the ZrN, ZrB_2 , and Si_3N_4 phase content, we generate structure models via melt-quench and subsequent annealing techniques. We will show that formation of nm-sized ZrN and ZrB_2 nuclei happens even at the short time-scales of our computer simulation. We compute elastic moduli and Vickers hardness and highlight the impact of Si_3N_4 addition to ZrSiBCN materials.

2. 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 ZrB_2 , ZrN, ZrC, and Si_3N_4 . For example, models with composition $\text{Zr}_{42}\text{B}_{32}\text{C}_8\text{N}_{18}$ are initially set to a density of 6.0 g/cm^3 , and adding Si_3N_4 lowers the density accordingly. Then we create a “liquid” state via simulation at 5000 K for 10 ps (5000 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 $5 \cdot 10^{13} \text{ Ks}^{-1}$) and finally down to 300 K in 20 ps (cooling rate of $8.5 \cdot 10^{13} \text{ Ks}^{-1}$). 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 Fig. 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 $2.5 \times 10^{14} \text{ Ks}^{-1}$, while keeping the temperature constant for 5–20 ps once the desired temperature has been achieved. A graph with the temperature profile during simulated annealing is shown in Fig. 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 configurations track 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 Fig. 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].

3. Results

3.1. Composition diagram

We investigate ZrSiBCN structures with composition located in the quaternary ZrB_2 -ZrN-ZrC- Si_3N_4 phase diagram. Every model comprises of 100 atoms. We compute mole coefficient and mole fraction (mol%) directly from composition, e.g. $\text{Zr}_{25}\text{Si}_{18}\text{B}_{16}\text{C}_8\text{N}_{33} = 8 \cdot \text{ZrC} + 9 \cdot \text{ZrN} + 8 \cdot \text{ZrB}_2 + 6 \cdot \text{Si}_3\text{N}_4 = 25.8 \text{ mol}\% \text{ ZrC} + 29.0 \text{ mol}\% \text{ ZrN} + 25.8 \text{ mol}\% \text{ ZrB}_2 + 19.4 \text{ mol}\% \text{ Si}_3\text{N}_4$. We fix the amount of ZrC in all models (8 formula units of ZrC) and represent the composition of the remaining ZrB_2 -ZrN- Si_3N_4 content in a ternary diagram (Fig. 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 ZrB_2 -like fragments).

Starting from the “parent” composition of $\text{Zr}_{42}\text{B}_{32}\text{C}_8\text{N}_{18}$

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