In Search of Amorphization-Resistant Boron Carbide

Ghatu Subhash^{a,*}, Amnaya P. Awasthi^a, Cody Kunka^a, Phillip Jannotti^b, Matthew DeVries^a^aMechanical and Aerospace Engineering, University of Florida, Gainesville, FL, 32611, USA^bArmy Research Laboratories, Aberdeen Proving Grounds, Aberdeen, MD, 21005, USA

Abstract

Despite its superior mechanical properties, boron carbide suffers from amorphization, a pressure-induced phenomenon that disturbs crystalline order and likely reduces shear strength. Numerous experimental and computational studies have investigated the structure and origins of amorphization, yet strategies to mitigate this deleterious phenomenon elude. However, recent investigations have revealed three new research avenues for addressing this issue. First, we identify crystallographic cage spaces that may accommodate foreign atoms to potentially prevent structural collapse. Second, we propose polymorph-level tailoring through strict control of processing conditions. Finally, we demonstrate that reducing grain size to nanometer scale increases hardness and may counter amorphization.

Keywords: Boron carbide, polymorph, amorphization resistance, Raman spectra, cage-space, DFT

Superhard materials possess hardness above 40 GPa and serve as prominent contenders in manufacturing of abrasives, polishing/cutting tools, armor, and wear-resistant coatings. Of these materials, boron-based compounds, such as boron carbide (B₄C), boron suboxide (B₆O), boron nitride (BN), and several boron phases (e.g., α and β phases) are the most promising. Among these, boron carbide has received considerable attention because its combination of low mass density, high hardness, and high strength is attractive for impact applications. However, an anomalous deformation behavior known as “solid-state amorphization” occurs under extreme pressures (e.g., those of high-velocity impacts), bereaves boron carbide of its structural integrity, and limits its engineering utility. Through shock experiments, Grady [1] was the first to contrast the post-yield softening (loss of shear strength beyond Hugoniot elastic limit (HEL)) of boron carbide with the post-yield hardening of silicon carbide. He attributed this softening to inhomogeneous deformation in B₄C, but did not specify the exact mechanism. Later, Chen et al. [2] identified this deformation mechanism as localized amorphization (loss of crystalline order) by conducting

transmission electron microscopy (TEM) of small fragments of B₄C armor plates subjected to ballistic impact. Since then, this mechanism has been observed under indentation [3–5], ballistic impact [2, 6], laser shock [7], diamond anvil cell [8], mechanical scratching [9], electric fields [10], and radiation [11]. Numerous characterization techniques, such as TEM [2, 7], Raman spectroscopy [4, 12–14], photoluminescence [14], FTIR [14], EELS [2], and neutron scattering [3], have been employed to observe the structure of the amorphized region. The consequences of amorphization include reduced ballistic performance [2], loss of hardness under dynamic loads [14–16], post-HEL softening [1], and change in electrical properties [10]. In recent years, advances in atomistic modeling [17–21] have shed additional light on amorphization as well. This manuscript summarizes the state-of-the-art advancements in understanding this phenomenon and the attempts in developing counter mechanisms. Finally, new avenues and future directions are proposed with the ultimate goal of eliminating amorphization to enhance the strength and hardness of boron carbide.

Amorphization in boron carbide can be described as the inhomogeneous loss of crystalline order in small zones scattered within a volume influenced by a high-pressure event [2–5, 7, 8]. Examples of these zones formed beneath an indentation are shown in the TEM images of Figure 1. Amorphization manifests on two

*Corresponding author. P. O. Box 116250 Gainesville, FL 32611.

Email addresses: subhash@ufl.edu (Ghatu Subhash), amnaya@ufl.edu (Amnaya P. Awasthi), ckunka@ufl.edu (Cody Kunka), phillip.a.jannotti.ctr@mail.mil (Phillip Jannotti), mdevries1120@ufl.edu (Matthew DeVries)

Figure 1: (a) Transmission electron microscopy revealing amorphization bands and a crack beneath indentation on a boron carbide sample. (b) Magnified region (R) showing dispersed amorphization zones. (c) and (d) are higher magnifications in the vicinity of amorphization zones and show lattice-level details, including dislocations and lattice rotation. Lattice dislocations are indicated by solid circles.

distinct length scales: micron-length, slender bands that spread far from the indentation tip (Figure 1(a)) and nanometer-length regions dispersed close to the indentation tip (Figure 1(b)). The zones contain numerous dislocations (Figures 1(c) and 1(d)) that induce lattice rotations and shear-displacements. These features demonstrate that amorphization is a shear-driven process [4, 22, 23]. The occurrence of amorphization can also be detected by the presence of peaks at 1340 cm^{-1} , 1520 cm^{-1} , and 1810 cm^{-1} in the Raman spectrum [4, 14, 23]. Because these peak locations are similar to the Raman spectra of carbon-based compounds [3–5, 14], many investigations posit that such compounds form as a result of amorphization. For example, scratch testing [9], which induces high temperatures and shear stresses, produced an amorphous matrix with carbon nanotubes and nanowires. In another study, carbon rings were identified in amorphized boron carbide [8]. At the atomistic level, amorphization can be described as a rearrangement of bonding among constituent atoms [24, 25]. This rearrangement is reversible through annealing; for example, the disappearance of amorphous peaks and reemergence of crystalline peaks were ob-

served by heating amorphized boron carbide above 600 K [12].

Numerous factors complicate attempts to explain the amorphization process. While boron carbide is generally thought to have the rhombohedral crystal structure with space group 166 ($R\bar{3}m$), the number and arrangement of the carbon and boron atoms in the unit cell may vary [26, 27]. Further, because the formation energies of many of these possible polymorphs are within a narrow range, fabricated samples may comprise multiple crystal structures [24, 27, 28]. In general, $(B_{11}C_p)CBC$ is considered the predominant polymorph [24, 26, 27, 29–34], but other polymorphic constituents are frequently debated [27, 29, 35]. In addition to uncertainty in virgin structure, kinetics and energetics of the amorphization process are not fully established. Trends in Gibbs free energies calculated from density functional theory (DFT) [24] and compressive responses calculated from *ab-initio* simulations [36] were used to suggest that the $(B_{12})CCC$ is the key precursor to amorphization. These studies have also shown that the boron icosahedra retain their structural integrity after amorphization and that the primary mechanism responsible for initiating amor-

phization is bending of the linear chains [17, 22]. This finding is consistent with an experimental study that analyzed the orientations of shear bands relative to that of the linear chains. The amorphous bands were found to mainly form parallel to the (113) and (2 $\bar{1}$ 3) planes [2]. However, another work [37] used DFT and enthalpy calculations to attribute amorphization to chain inhomogeneity. In this explanation, vacancy-containing carbon chains, C-□-C, stochastically produced below HEL transform into C-C chains above HEL, and the resulting discontinuous volume distribution causes stress concentrations that lead to amorphization. This mechanism is consistent with the finding that uniform (B₁₁C_p)CC exhibits significantly higher mechanical strength than (B₁₁C_p)CBC [38]. Finally, the existence of twinning in boron carbide complicates understanding of the failure process. Under high shear deformation, activation of the (0001)<1010> slip system forms twins and eventually amorphous bands [18]. The propensity for twinning has been shown to be polymorph-driven [19].

Efforts to minimize amorphization have mostly been focused on doping boron carbide with foreign atoms and forming composites. DFT analyses [39] for (B₁₂)CBC and (B₁₂)CCC revealed that Be, Mg, Al and Si preferred chain centers for substitution while N, P and S preferred chain ends; for (B₁₁C_p)CBC, Si favored polar icosahedral sites. Experimentally, doping with silicon in the icosahedra has roughly doubled the pressure required for amorphization to 67 GPa [40]. This improved stability was attributed to a 91% reduction in the propensity for formation of (B₁₂)CCC through atom swapping. It was also found that boron carbide with Si-Si chains doubled the critical strain and slightly lowered mass density and hardness as compared to pristine boron carbide [17]. However, another study showed that doping with silicon increased flexural strength, fracture toughness, and hardness [41]. Simulated shear deformations [42] along (001)<100> revealed that the icosahedra in B₆O, B₁₂P₂, and B₄C are quite strong but that the three-atom chains in B₄C are far weaker and more brittle than the two-atom chains in B₆O and B₁₂P₂. Hence, Tang and coworkers [43] showed that a composite with alternating layers of B₄C and B₆O exhibited a 40% improvement in strength as compared to single-phase B₄C.

While previous efforts to increase amorphization resistance in boron carbide encompassed substitutional doping and formation of boron-carbide composites, we present new avenues based on an in-depth understanding of the crystal structure. The first of these paths addresses the large volume of low electron-density space (“cage space”) that we have identified in the boron-carbide lattice through DFT modeling (see electron-

density map in Figure 2(a)). The presence of these cage spaces may rationalize the fact that the melt [44] and the amorphous phase [45] have higher mass density than the solid phase. Closer examination of the crystal structure shows that these continuous cage spaces are located in specific crystallographic locations (i.e., part of the extended lattice) and are different from imperfections, cavities, or vacancies. Interestingly, this cage space is adjacent to linear chains, which have higher susceptibility to bending than icosahedra. Upon application of load, the chains have a higher propensity to bend into the cage spaces due to lack of atomic support in their immediate neighborhood. Additional deformation may create new bonding among bent chains and icosahedra and hence advance amorphization. Thus, we propose that filling the cage spaces with suitable additives represents an avenue for developing amorphization-resistant boron carbide (ARBC). By supporting the chains, these additives decrease susceptibility for chain bending and hence increase amorphization resistance. However, the simulation domain includes a large number of polymorphs [27] and a large number of admissible additive atoms. Given the varying degrees of participation of different boron-carbide polymorphs in amorphization [24], the most susceptible polymorphs could be targeted. As an example of additive selection, we present relaxed crystal structure of nickel-doped B₄C (Figure 2(b)) from DFT (simulation parameters similar to [27]). Figure 2(c) shows increased stiffness (curvature of strain energy) of homogeneous compression of this doped structure as compared to pristine B₄C. Selection of additive atoms requires consideration of atomic size, electronegativity, and thermodynamic stability (see Figure 2(d)). Difficulty in stabilizing single-atom species may suggest use of ions instead of single atoms. Balance must be sought between decreasing amorphization susceptibility and increasing overall mass density of this new cage-doped boron carbide. Theoretical studies on stability under deformation (e.g., [18, 25, 36, 42]) will be required to predict the relative favorability, stability, and performance of cage-doped boron carbide.

The second avenue to increase amorphization-resistance in boron carbide is to fabricate polymorphs with greatest thermodynamic and mechanical stability. Because numerous polymorphs possess similar Gibbs free energies of formation [24], even small variations in processing conditions can produce multiple polymorphs with different properties in the same sample. It is speculated that the inhomogeneous nature of amorphization (Figure 1) is partly due to the random distribution of weak polymorphic phases. Our DFT calculations have identified ten groups of polymorphs catalogued by lo-

Figure 2: (a) Isosurfaces (3-D contour maps) representing high (yellow) and low (blue) levels of spatial distribution of electron density in boron-carbide crystal structure. White areas represent regions with electronic density below 20% of the maximum value and are termed “cage spaces.” Red arrows depict how the chains are susceptible to bending/buckling into cage-spaces. These spaces are continuous, and their sizes are sufficient to accommodate additive atoms. Green atoms are boron while brown are carbon. (b) Ni-cage-doped B₄C used for DFT modeling. (c) DFT results of relative performance in volumetric compression for pristine and Ni-cage-doped B₄C. (d) Electronegativity versus atomic radius of single atoms of different elements of the periodic table.

Figure 3: (a) Representative polymorphs of B₄C groups catalogued by lattice parameters, energy, and Raman spectra [27]. (b) Relative energies of the different polymorphic groups. (c) Combined Raman spectrum using weighted superposition of four constituent B₄C polymorphic groups; weights are shown in inset.

Figure 4: Spatial Raman map illustrating the amorphization intensity within the indented regions of (a) coarse-grained and (b) ultrafine-grained boron carbide. The indentation load was 7.36 N for both materials. Degree of amorphization is significantly less in ultra-fine material compared to that of coarse-grained.

cal bonding environment in Figure 3(a). They have distinct potential energies (Figure 3(b)), lattice parameters, Raman spectra [27], and susceptibilities to amorphization [24]. However, the ability to identify the presence, abundance, and distribution of these polymorphs is currently not available. Our recent quantum-mechanical simulations of Raman spectra on multiple polymorphs [27] shed light in building polymorph-tailored composites with customizable properties. For example, Figure 3(c) compares a superposition of simulated Raman spectra from four polymorphs to an experimental scan from hot-pressed boron carbide. This choice of polymorphs is not only consistent with many prior studies [24, 30, 33, 46], but the superposition approach also allows predicting relative abundances. While the major features of the experimental spectrum are adequately captured, missing features could be attributed to additional crystal structures, including those which are not Raman-active. Hence additional techniques, such as nuclear-magnetic resonance and infrared spectroscopy, may prove useful to completely describe polymorph identification and variability. Development of polymorph-driven ARBC mandates not only the ability to identify constituents but also the capability to fabricate them. Strict control of processing conditions will be required to preferentially produce desired polymorphs. These advances in processing may also enable tailoring of mechanical, thermal, and electronic properties of boron carbide for a variety of applications.

The third potential means of synthesizing ARBC is reduction of grain size to nanometers. A recent experimental study [16] showed that 300-nm-grain-size

boron carbide produced substantially higher hardness and lower propensity for amorphization than a 10- μ m-grain-size counterpart. Extent of amorphization is represented by spatially mapping area under the 1340- cm^{-1} amorphous peak of the Raman spectrum obtained from the indented surface as shown in Figure 4. This result implies that reduction in grain size can curb the propensity for amorphization by limiting the strain that can be accommodated in a grain. Such a microstructural-design approach may lead to preferential activation of different mechanisms, such as cracking and/or dislocations, instead of amorphization. To fully exploit the potential of grain-size reduction, in-depth understanding of the relationship between grain size and associated deformation mechanisms must be pursued. Finally, challenges associated with processing nano-grained boron-carbide powder and preventing grain growth during sintering must be resolved.

Amorphization-resistant boron carbide is sought for excellent strength and hardness. This article has summarized state-of-the-art experimental and computational efforts in understanding and mitigating amorphization in boron carbide. Thus far, most experimental approaches have been unsuccessful in developing fully amorphization-resistant boron carbide. However, we have shown that grain-size refinement significantly reduces the propensity of amorphization and increases hardness. While previous computational works have shown promise, none has fully deciphered the root-cause of and inherent susceptibility for amorphization in boron carbide. In this manuscript, we have highlighted the predominance of cage spaces within the crystal structure of boron carbide through DFT-level analysis of spatial distribution of electronic density. The existence of these cage spaces may not only explain the discrepancy between mass densities of solid and melt phases of boron carbide but could also be responsible for driving amorphization through chain bending. We propose that development of ARBC can be accomplished by filling the cage spaces with compatible atomic species. Alternatively, ARBC could be developed by forming stable polymorphs and eliminating phases that are more susceptible to amorphization. This approach requires fine-tuning polymorphic variability through stringent control of processing methods. Such fabrication techniques could also be useful in tailoring boron carbide for multifunctional applications.

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Amorphization-resistant boron carbide

Tailoring polymorphic variability

Using nanosize grains