



## Viewpoint Article

## In search of amorphization-resistant boron carbide

Ghatu Subhash<sup>a,\*</sup>, Amnaya P. Awasthi<sup>a</sup>, Cody Kunka<sup>a</sup>, Phillip Jannotti<sup>b</sup>, Matthew DeVries<sup>a</sup><sup>a</sup> Mechanical and Aerospace Engineering, University of Florida, Gainesville, FL 32611, USA<sup>b</sup> Army Research Laboratories, Aberdeen Proving Grounds, Aberdeen, MD 21005, USA

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## 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.

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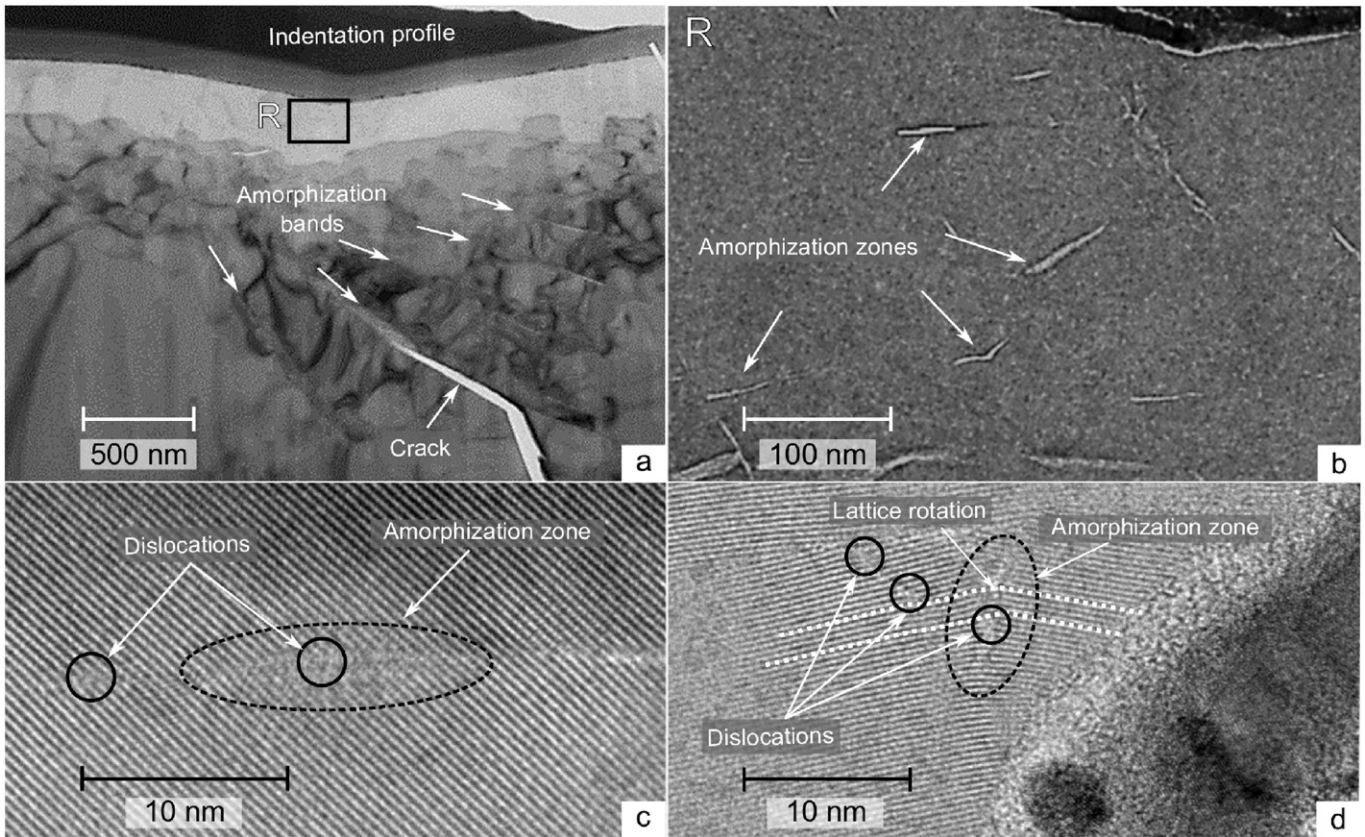
Superhard materials possess hardness above 40 GPa and serve as prominent contenders in manufacturing of abrasives, polishing/cutting tools, armor, and wear-resistant coatings. Of these materials, boron-based compounds, such as boron carbide ( $B_4C$ ), boron suboxide ( $B_6O$ ), boron nitride (BN), and several boron phases (e.g.,  $\alpha$  and  $\beta$  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  $B_4C$ , 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  $B_4C$  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 Fig. 1. Amorphization manifests on two distinct length scales: micron-length, slender bands that spread far from the indentation tip (Fig. 1(a)) and nanometer-length regions dispersed close to the indentation tip (Fig. 1(b)). The zones contain numerous dislocations (Fig. 1(c) and (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  $1340\text{ cm}^{-1}$ ,  $1520\text{ cm}^{-1}$ , and  $1810\text{ cm}^{-1}$  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

\* Corresponding author at: P. O. Box 116250, Gainesville, FL 32611, USA.

E-mail addresses: [subhash@ufl.edu](mailto:subhash@ufl.edu) (G. Subhash), [amnaya@ufl.edu](mailto:amnaya@ufl.edu) (A.P. Awasthi), [ckunka@ufl.edu](mailto:ckunka@ufl.edu) (C. Kunka), [phillip.a.jannotti.ctr@mail.mil](mailto:phillip.a.jannotti.ctr@mail.mil) (P. Jannotti), [mdevries1120@ufl.edu](mailto:mdevries1120@ufl.edu) (M. DeVries).



**Fig. 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.

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 observed 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  $(B_{12})CCC$  is the key precursor to amorphization. These studies have also shown that boron icosahedra retain their structural integrity after amorphization and that the primary mechanism responsible for initiating amorphization 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,  $C-\square-C$ , 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  $(B_{11}C_p)CC$  exhibits significantly higher mechanical strength than  $(B_{11}C_p)CBC$  [38]. Finally, the existence of twinning in boron carbide complicates understanding of the failure process. Under high shear deformation, activation of the  $(0001)\langle 1010 \rangle$  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  $(B_{12})CBC$  and  $(B_{12})CCC$  revealed that Be, Mg, Al and Si preferred chain centers for substitution while N, P and S preferred chain ends; for  $(B_{11}C_p)CBC$ , 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  $(B_{12})CCC$  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  $(001)\langle 100 \rangle$  revealed that the icosahedra in  $B_6O$ ,  $B_{12}P_2$ , and  $B_4C$  are quite strong but that the three-atom chains in  $B_4C$  are far weaker and more brittle than the two-atom chains in  $B_6O$  and  $B_{12}P_2$ . Hence, Tang and coworkers [43] showed that a composite with alternating layers of  $B_4C$  and  $B_6O$  exhibited a 40% improvement in strength as compared to single-phase  $B_4C$ .

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

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