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Nanotwins soften boron-rich boron carbide ($B_{13}C_2$)

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Extensive studies of metals and alloys have observed that nanotwins lead to strengthening, but the role of nanotwins in ceramics is not well established. We compare here the shear strength and the deformation mechanism of nanotwinned boron-rich boron carbide ($B_{13}C_2$) with the perfect crystal under both pure shear and biaxial shear deformations. We find that the intrinsic shear strength of crystalline $B_{13}C_2$ is higher than that of crystalline boron carbide ($B_4C$). But nanotwins in $B_{13}C_2$ lower the strength, making it softer than crystalline $B_4C$. This reduction in strength of nanotwinned $B_{13}C_2$ arises from the interaction of the twin boundary with the C-B-C chains that connect the $B_{12}$ icosahedra. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4978644]

Boron carbide ($B_4C$) is of great interest because of its promising properties of low density, superhardness, thermal stability, and high elastic Hugoniot limit.$^{1-5}$ However, engineering applications of $B_4C$ to body armor or abrasive powders have been impeded by the high pressure brittle failure due to amorphous shear band formation.$^{6-8}$ We recently used atomistic simulations to show that amorphous shear band underlyng the brittle failure in $B_4C$ arises from fracture of the $B_{13}C$ icosahedra which increases the density of the amorphous band compared to nearby crystalline regions, leading to tension that induces cavitation and then failure.$^9$ Under realistic conditions, defects such as twinning and grain boundaries might play important roles in determining the mechanical properties and failure mechanism of $B_4C$ and related materials.$^{10,11}$ In particular, the ubiquitous existence of twins in these materials has motivated studies of their impact.$^{12-15}$ Indeed, we recently used both theory and experiment to examine the twin structures in $B_4C$ and boron-rich boron carbide ($B_{13}C_2$).$^{14}$ In addition, the nanotwins in $B_4C$ could strengthen the materials by suppression of twin boundary (TB) slip within the nanotwins.$^{15}$ However, the mechanism by which these nanotwinned structures determine mechanical properties is not fully understood at the atomistic scale, especially for $B_{13}C_2$. Although some experimental observed planar defects in $B_{13}C_2$ may be Wadsley type defects such as stacking faults, we do not consider them in current study because the atomistic structures for these defects are not identified.

Boron carbide exhibits a wide range of carbon solid solubilities ranging from ~8 to ~20 at. %.$^2$ In particular, it is of interest to understand how the properties of $B_{13}C_2$ are compared to $B_4C$. To explain the stoichiometry of $B_{13}C_2$, structures such as $B_{12}(BBC)$, $B_{12}(CBC)$, and $B_{12}(BBB)B$ have been proposed.$^{16-18}$ Previous QM simulations predicted that the $B_{12}(CBC)$ is the lowest energy structure among all the possible variations of the basic $B_4C$ structure.$^{19}$ Indeed, the experimental Raman spectrum is consistent with the $B_{12}(CBC)$ predicted structure,$^{20}$ indicating this to be the most plausible structure for B-rich boron carbide. Note that in discussing experiments we use the terms $B_{13}C_2$ and $B_4C$, whereas for the computations we use notations such as $B_{12}(CBC)$. This is because the experimentalists know for sure the overall compositions, but do not know which atoms are in the icosahedra and chains, whereas for the theory we use the specific distributions that correspond to the lowest energy.

We report here quantum mechanics (QM) simulations for the deformations of both perfect and twinned ($B_{12})CBC$, which we compare with ($B_{13}C_p)CBC$. We find that the shear strength of perfect ($B_{12})CBC$ is 17.7% higher than that of ($B_{13}C_p)CBC$ under pure shear deformations, while they are similar (within 0.4%) under indentation conditions. However, the presence of twins decreases the shear strength of perfect ($B_{12})CBC$ under both conditions, making it even softer than ($B_{13}C_p)CBC$. We find that the failure mechanism of twinned ($B_{12})CBC$ arises from the interaction of the C-B-C chain with the high energy twin boundary (TB). This allows the stress to achieve sufficient strain to cause construction of the ($B_{13})icosahedral cluster to be 21.6% smaller than for perfect ($B_{13})CBC$.

Our QM simulations use the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional with the projector augmented wave method for the core-valence interactions as implemented in the VASP package.$^{21-24}$ We found that a kinetic energy cutoff of 500 eV for the plane wave expansions gives excellent convergence of the total energies, energy differences, and structural parameters. The convergence criteria were set to $1 \times 10^{-6}$ eV energy difference for solving the electronic wave function and $1 \times 10^{-3}$ eV/Å force for geometry optimization. Reciprocal space was sampled using the Γ-centered Monkhorst-Pack scheme with a fine resolution less than $2\pi \times 1/60$ Å$^{-1}$ for geometry optimization.

We applied the pure shear deformation by fixing the shear strain at various values while relaxing the other five strain components.$^{25}$ To mimic the stress conditions under indentation experiments, we applied biaxial shear deformation where the ratio of the compressive stress beneath the indenter normal to the chosen shear plane has a fixed fraction.
of the tangential stress while the other four strain components are relaxed. Here, we set the centerline-to-face angle to 68° to mimic the Vickers indenter. The residual stresses after relaxing were less than 0.5 GPa for pure shear and biaxial shear deformation.

Fig. 1(a) displays the B12(CBC) crystal structure with R3m space group where the B12 icosahedral cluster is located on the corner and the C-B-C chain is along the [111]r directions. Here, the subscript “r” represents the rhombohedral cell. To examine how the twinned structure changes the mechanical properties of the perfect B12(CBC), we constructed the twinned structure with the twin boundary along the {100}r plane as shown in Fig. 1(b). Details of this twinned structure were discussed previously. The QM predicts a twin interfacial energy of 40.6 mJ/m² for B12(CBC), which is much lower than the 83.2 mJ/m² for symmetric B11Cp(CBC). This much lower interfacial energy for B12(CBC) might arise from the easier accommodation of B12 icosahedra along the twin boundary compared with B11C icosahedra. This low TB energy might explain why twin planar defects are pervasive in B13C2, whereas it is possible to form twin-free grains in B4C that are micrometers across.

Our previous studies showed that the easiest shear slip system for B4C is (001)r/001>, which parallels the amorphous shear band observed in experiments. For B12(CBC), we performed pure shear deformation along the same slip system. For the twinned B12(CBC), we shear along the TB which is along the {001}r plane of perfect B12(CBC). The stress-strain relationships for these two structures are displayed in Fig. 2, and compared with the perfect B11Cp(CBC) crystal examined previously. The maximum shear stress for perfect B12(CBC) is 45.8 GPa, which is 17.7% higher than the strength limit of B4C (38.9 GPa), indicating that the intrinsic strength limit is higher for perfect B12(CBC) than for B11Cp(CBC). However, the shear strength of twinned B12(CBC) decreases to 35.9 GPa, which is 21.6% lower than that of perfect B12(CBC) and 7.7% lower than that of perfect B12(CBC). The critical shear stress for B12(CBC) and B11Cp(CBC) is summarized in Table I. The B12(CBC) directly fails after the maximum shear stress as shown in Fig. 2, indicating that it does not experience any “plastic” deformation. In contrast, B11Cp(CBC) does exhibit “plasticity,” of 12.1%, in the infinite slow shear deformation at 0 K along the most plausible slip system (001)jr/(001)r, as shown in Fig. 2.

To understand the softening effect from nanotwins in B12(CBC) and to illustrate amorphous band formation at high strain, we examined the structural changes in perfect and twinned B12(CBC), as shown in Fig. 3. For perfect B12(CBC), the structure deforms continuously as the strain increases to 0.331 without bending the C-B-C chain, as shown in Fig. 3(b). But with a strain of 0.348, we find that B12(CBC) fails catastrophically, as shown in Fig. 3(b). This differs from the failure mechanism of B4C, which involves a two-step procedure: (1) the B-C bond between icosahedra is stretched and broken to form a reactive carbene; (2) the system then displays plastic deformation for an additional 0.122 strain until at 0.331, in which the C-B-C chain has bent sufficiently for the carbene to react with the middle B of the chain, resulting in destruction of icosahedron with concomitant formation of the amorphous band. The first step at 0.209 strain for B11Cp(CBC) releases the stress, decreasing the maximum shear strength below that for the perfect B12(CBC).

For twinned B12(CBC), the stress-strain slope is 4.4% lower than for perfect B12(CBC), indicating a lower shear modulus, which arises from the presence of the high energy TBs. As shear stress is applied to the twinned B12(CBC), the C-B-C chains in the lower half start to bend towards the icosahedral clusters along the TBs before failure, as shown in Fig. 2.

TABLE I. Critical shear stress for B11Cp(CBC) and B12(CBC) under pure and biaxial shear deformation. The data for symmetric twinned B11Cp(CBC) are from Ref. 15.

<table>
<thead>
<tr>
<th>Critical shear stress (GPa)</th>
<th>B11Cp(CBC)</th>
<th>B12(CBC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perfect (pure shear)</td>
<td>38.9</td>
<td>45.8</td>
</tr>
<tr>
<td>Twin (pure shear)</td>
<td>43.6</td>
<td>35.9</td>
</tr>
<tr>
<td>Perfect (biaxial shear)</td>
<td>28.5</td>
<td>28.6</td>
</tr>
<tr>
<td>Twin (biaxial shear)</td>
<td>31.8</td>
<td>26.0</td>
</tr>
</tbody>
</table>

FIG. 1. The structure of B12(CBC) and its twin structure from QM prediction: (a) QM predicted structure for B12(CBC). (b) QM predicted structure for twinned B12(CBC) with 2 crystal layers between twin boundaries. The boron and carbon atoms are represented by green and cyan balls, respectively.

FIG. 2. The shear-stress shear-strain relationship of B12(CBC), twinned B12(CBC), and B11Cp(CBC) along the least stress slip system.
As the strain increases to 0.299, the C-B-C angle bends to 165.3° and the middle B is 1.93 Å from the cage B. With further shear to 0.322 strain (Fig. 3(d)), the middle chain boron is only 1.75 Å from the cage B, leading to B-B bond formation that deconstructs partially the icosahedron (rectangular region of Fig. 3(d)), and leading to shear stress release from 35.9 GPa to 30.8 GPa. With further shear to 0.392 strain, the cages along the TBs and the nearby chains become fully deconstructed with the shear stress decreasing to 15.3 GPa, as shown in the rectangular region of Fig. 3(e).

The stress conditions under indentation experiments are very complex compared with our simulated pure shear deformation. To predict the material behavior under indentation experiments, we performed biaxial shear deformation to mimic the stress conditions under indentation.26 The stress-strain relationships for the perfect and twinned B12(CBC) are shown in Fig. 4(a). For perfect B12(CBC), the maximum shear stress is 28.6 GPa, which is only slightly higher than that of the B11Cp(CBC) (28.5 GPa). This indicates that the hardness of perfect B12(CBC) should be close to B11Cp(CBC). However, for twinned B12(CBC), the maximum shear stress decreases to 26.0 GPa, which is 9.1% lower than perfect B12(CBC) and 8.8% lower than B11Cp(CBC). The critical shear stress under biaxial shear deformation is summarized in Table I.

The mechanism of deformation for twinned B12(CBC) under biaxial shear deformation is displayed in Figs. 4(b) and 4(c). As a compressive stress is applied, the C-B-C chains bend by 50.3° over the whole simulation cell. As the shear strain increases to 0.276, the C-B-C chains next to the TBs bend from 180° to 129.7°. As the shear strain increases to 0.299, the C-B-C chain bends to 124.5°, decreasing the distance from the B of the C-B-C chain to the B of the icosahedron to 1.64 Å, This leads to the failure of the cluster along the TBs, which is similar to the process under pure shear deformation.
Our previous study\textsuperscript{15} showed that nanotwins in B\textsubscript{11}C\textsubscript{p}(CBC) increase the strength compared to the perfect B\textsubscript{11}C\textsubscript{p}(CBC) because the presence of twins suppresses the stress decrease as the B-C bond between icosahedral clusters breaks. However, the nanotwins in B\textsubscript{12}(CBC) decrease the strength of the perfect crystal because the failure mechanism of B\textsubscript{12}(CBC) does not involve the B-C bond breaking between icosahedra. The high interfacial energy of the twin makes the interaction of C-B-C chain with icosahedra easier to proceed in the twinned B\textsubscript{12}(CBC). Thus, although B\textsubscript{12}(CBC) has a very similar twin structure to B\textsubscript{11}C\textsubscript{p}(CBC), the twins play quite different roles in these two materials due to the difference in the failure mechanisms. To improve the strength of B\textsubscript{12}(CBC), one needs to design this material to have lower twin densities, which is opposite to B\textsubscript{11}C\textsubscript{p}(CBC).

Niihara \textit{et al.} reported that, for chemical vapor deposited (CVD) boron carbide, both hardness and fracture toughness decreases over 18.0\% as the boron content increases.\textsuperscript{27} However, mechanical test on hot-pressed boron carbide indicated that boron addition did not significantly affect elastic modulus, flexural strength, hardness, and fracture toughness.\textsuperscript{28,29} The latter two experiments on hot pressed boron carbide are consistent with our theoretical prediction that the critical failure stress for B\textsubscript{13}C\textsubscript{2} and B\textsubscript{4}C are similar (changes <1.0\%) under biaxial shear deformation.

In summary, we use QM simulations to examine deformations of both twinned and nontwinned B\textsubscript{12}(CBC) under both pure shear and biaxial shear conditions, which we compare with deformation of both perfect B\textsubscript{11}C\textsubscript{p}(CBC) and its twin. Some main conclusions are as follows:

- The twin interfacial energy of B\textsubscript{12}(CBC) is 40.6 mJ/m\textsuperscript{2}, which is \~1/2 value for symmetric twins in B\textsubscript{11}C\textsubscript{p}(CBC).
- Perfect B\textsubscript{12}(CBC) has a higher shear strength than B\textsubscript{11}C\textsubscript{p}(CBC) under pure shear conditions. The reason is that the presence of twins in B\textsubscript{12}(CBC) lowers the shear strength, making it softer than B\textsubscript{11}C\textsubscript{p}(CBC). The failure mechanism for twinned B\textsubscript{12}(CBC) involves the interaction of the C-B-C chain with the icosahedra along the TBs.
- Under biaxial shear conditions, perfect B\textsubscript{12}(CBC) has a shear strength similar to B\textsubscript{11}C\textsubscript{p}(CBC). But twinned B\textsubscript{12}(CBC) has a lower shear strength than perfect B\textsubscript{12}(CBC) or B\textsubscript{11}C\textsubscript{p}(CBC). The failure mechanism of twinned B\textsubscript{12}(CBC) under biaxial shear deformation is similar to the mechanism under pure shear deformation.

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