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Nanotwinning and amorphization of boron suboxide

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ABSTRACT

Recently, researchers discovered that in contrast to isolated twins, periodic twins with nanoscale spacing can dramatically improve mechanical properties. Ceramics engineers now seek to incorporate this "nanotwinning" into icosahedral solids because of their high strength, high stability, and low mass density. In this manuscript, we assert that boron suboxide, while far less studied than boron carbide (i.e., the most popular icosahedral solid), possesses higher propensity for nanotwinning and higher theoretical promise. For boron suboxide, the influence of processing on twin spacing is explored through mechanical testing and transmission electron microscopy. Quantum-mechanical simulations are then performed to suggest a critical twin spacing that would maximize performance and to show how to track experimental nanotwinning with x-ray diffraction. Finally, transmission electron microscopy and Raman spectroscopy show that amorphization, the localized loss of crystallinity, drives mechanical failure in ways unique to boron suboxide.

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1. Introduction

Twins are crystallographic defects represented by a reflection of a parent lattice. They can occur during nucleation, growth, phase transformation, recrystallization, annealing, or deformation. Regardless of origin, twins generally induce stress concentrations that promote crack nucleation and lower mechanical performance [1]. However, recent investigations showed that increasing twin density (i.e., reducing twin spacing, λ) at the nanoscale can dramatically increase mechanical properties even beyond those of nanograined structures [2,3]. Nanotwinned copper (nt-Cu) produced by pulsed electrodeposition exhibited an order-of-magnitude increase in yield strength over regular copper (i.e., 900 vs. 70 MPa) without lowering electrical conductivity [4,5]. A later study showed nt-Cu had up to an 85% increase in fatigue strength (i.e., 370 vs. 80 MPa) [6]. Nanotwinned cubic boron nitride (nt-c-BN, $\lambda \approx 3.8$ *nm*) produced from onion nanoparticles exhibited a 40% increase in microhardness (>100 GPa) and a 140% increase in fracture toughness (>12 MPa $m^{1/2}$) [7,8]. Also produced from onion nanoparticles, nanotwinned diamond (nt-D, $\lambda \approx 5$ *nm*) reached a 200-GPa record hardness and showed improved thermal stability [9].

The latest proposals for nanotwinning are two ceramics: boron carbide (nt-B_4C) [10–12] and boron suboxide (nt-B_6O or β-B_6O) [13–15]. Experimentally, both B_4C and B_6O have exhibited superhardness (i.e., microhardness above 40 GPa), low mass density (2.52 g/cm^3 for B_4C and 2.60 g/cm^3 for B_6O), and moderate fracture toughness (3.4 MPa $m^{1/2}$ for B_4C and 4.2 MPa $m^{1/2}$ for B_6O) [16–20]. Crystallographically, these materials share boron-based icosahedra but have important differences [see Fig. 1(a) and (b)]. B_4C has three-atom chains that connect icosahedra, but the oxygen atoms that bond icosahedra in B_6O do not form chains. Icosahedral carbons can break the sixfold-symmetry in B_4C but not in B_6O. Also, B_4C is highly susceptible to structural heterogeneity due to polymorphism [17,21] while B_6O is not [16]. These differences in crystal structure affect the orientation of planar defects, such as twins. In B_6O, the $\{100\}_r$ family of planes is preferred for twinning [14,15,22] while many factors, such as stoichiometry and processing, strongly affect the preferred planes in B_4C [12,23,24]. As explained later, we believe these differences make B_6O more structurally

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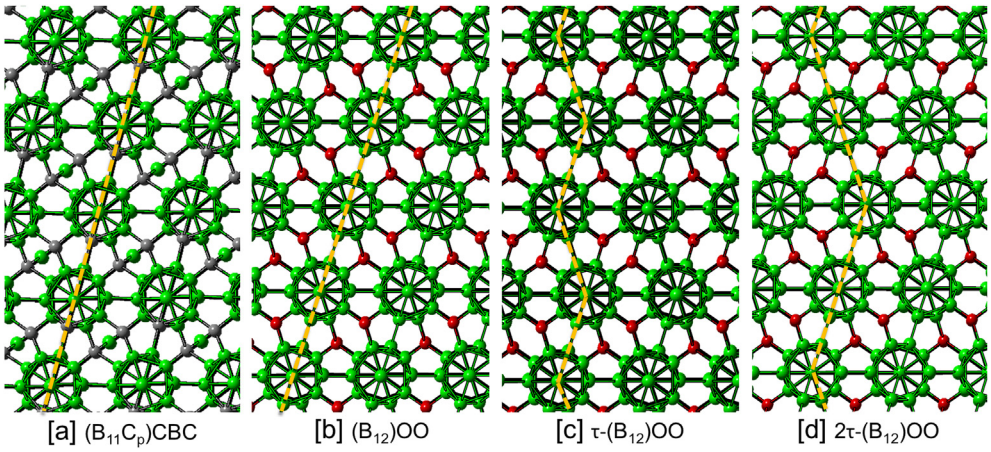

Fig. 1. The crystal structures of (a) $(B_{11}C_p)$CBC, (b) α-B_6O, (c) τ-B_6O, and (d) 2τ-B_6O share icosahedral fundamental units. Spheres are colored by element (i.e., green for boron, grey for carbon, and red for oxygen) and are sized according to covalent radius. Bends in the dashed yellow lines indicate twin planes. Note that the (a) C-B-C linear chains in B_4C are serially bonded while the (b–d) oxygen atoms in B_6O do not form chains. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

homogeneous and therefore a better candidate for nanotwinning. Hence, this manuscript focuses on B_6O but compares to B_4C when warranted.

Just as nanograining has a critical grain size that maximizes mechanical strength (i.e., Hall-Petch relationship), nanotwinning has a critical twin spacing (λ_{cr}). Both experimental [5,25] and theoretical [26–28] investigations on nanotwinned metals suggest that twin boundaries beneficially act as barriers to slip (i.e., dislocation motion) but deleteriously act as nucleation sites for partial dislocations. The balance of the effects of slip barriers and dislocation-nucleation sites is material-dependent and ultimately dictates λ_{cr}. Importantly, recognize that this mechanism was developed for metals. Ceramics, on the other hand, have strong chemical bonds that largely counter slip [29]. Regardless, some still argue that nanotwinning benefits ceramics by resisting slip [7,29]. Others argue that nanotwinning beneficially increases quantum confinement of bandgap energy of ceramics [7,30]. Few investigations of nanotwinned ceramics are available, so the correct mechanism may not have been speculated yet.

Determining λ_{cr} for B_6O represents a first step in demystifying the mechanism of nanotwinning in ceramics and in potentially achieving record properties for boron suboxide. To begin, a prior work established a new nomenclature for B_6O [14]. They retained the name of α-B_6O for the non-twinned structure but discarded β-B_6O and nt-B_6O for the nanotwinned structure. Instead, they proposed $i\tau$-B_6O where i represents the number of layers of icosahedra between twin boundaries. For example, τ-B_6O has twin boundaries separated by a single layer of icosahedra and a λ of approximately 0.44 nm [Fig. 1(c)]. Likewise, 2τ-B_6O has twin boundaries separated by two layers of icosahedra and a λ of approximately 0.89 nm [Fig. 1(d)]. That study also found that the DFT ground-state static energies of α-B_6O, τ-B_6O, 2τ-B_6O, 3τ-B_6O, and 4τ-B_6O were essentially equivalent. Therefore, we predict that experimentally varying twin spacing is feasible and that a fabricated sample could contain multiple regions with dissimilar twin spacings.

Apart from nanotwinning at critical spacing, countering solid-state amorphization represents the principal concern for maximizing the mechanical strength of many boron-rich icosahedral solids, including B_6O. In this deleterious mechanism, high pressures induce disordered bands at the nanoscale to concentrate stress and promote microcracking, post-yield softening, and catastrophic failure [17]. Before the present work, only two studies have experimentally observed amorphization of B_6O. They showed that nanoindentation induced amorphous bands with a width of 2–3 nm and a length of 200–300 nm mostly along $\{0\bar{1}11\}$ and $\{\bar{1}012\}$ [15,31]. Although no other experimental works covered the amorphization of B_6O, similarly sized amorphous bands were frequently found in B_4C [17,32–34]. In contrast to amorphization of B_6O, however, the amorphous bands in B_4C lay along numerous planes: $(11\bar{2}3)$ and $(2\bar{1}\bar{1}3)$ for ballistic impact [32], $(21\bar{3}5)$ and $(2\bar{2}01)$ for laser shock [35], $(31\bar{4}0)$ for hydrostatic depressurization [36], and many planes for indentation [33,37]. We believe this variety of preferred directions in B_4C is due to its aforementioned polymorphism-driven heterogeneity. Therefore, we expect less variety in the preferred directions for B_6O, which is much more homogeneous crystallographically. Regardless, the origins of amorphization, especially for B_6O, remain unclear.

The objective of this manuscript is to characterize and rationalize the mechanical response of nanotwinned B_6O. We first present the results of pulse-echo ultrasound, quasistatic/dynamic indentation, and quasistatic compression for both hot-pressed (HP) and spark-plasma-sintered (SPS) samples. To our knowledge, this is the first dynamic testing of B_6O. With scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HR-TEM), we explain the trends in properties through measurements of porosity, grain size, nanotwinning, and amorphization. We demonstrate that the twins and amorphous bands in B_6O heavily prefer certain crystallographic planes. We also employ Raman spectroscopy to investigate the uniqueness of the amorphization of B_6O. With experimental and quantum mechanical x-ray diffraction (XRD), we present a potential tool for quantifying the volume fraction of nanotwinning, which we believe to be beneficial to mechanical response. Finally, we perform biaxial shear simulations to suggest the critical twin spacing specific to B_6O.

2. Experimental

2.1. Materials

This study covers the two most popular high-pressure-high-temperature (HPHT) processing techniques for polycrystalline ceramics: hot pressing (HP) and spark plasma sintering (SPS). While both techniques mechanically apply uniaxial pressure, HP and SPS apply temperature through radiation and conduction, respectively. This difference in heating mechanism makes SPS significantly faster than HP and therefore can produce microstructural differences. The

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