Shear Amorphization of Boron Suboxide

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Abstract

We report for the first time the shear-induced local amorphization of boron suboxide subjected to nanoindentation. The amorphous bands have a width of ~1-3 nm and length of 200-300 nm along the (0 $\bar{1}$ 11) crystal plane. We show the direct experimental evidence that the amorphous shear bands of boron suboxide is driven from the coalescence of dislocation loops at high shear stresses. These observations provide the microscopic insights into the deformation and failure of the high-strength and lightweight ceramics.

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Super-hard materials with strong covalent bonds often fail in a brittle manner dominated by normal stresses at room temperature. The low-density boron suboxide (B_6O) is one of the super-hard materials with the hardness comparable to boron carbide (B_4C) and cubic boron nitride (BN) ceramics [1-5]. The unusual hardness of B_6O comes from its basic structure that composes of icosahedra (B_{12}) and two oxygen (O-O) atom chain at the center of the rhombohedral, which is similar to 12-atom icosahedra and a three-atom chain distribution in B_4C [6-10]. Unlike B_4C and BN that have been widely used in industry, B_6O have not been commercialized so far partially because of the difficulty in obtaining full densification using conventional sintering methods. Therefore, the basic properties of this ceramic material have not been completely studied [4, 11-13]. The potential applications of the B_6O ceramic in wear and hard facing parts could be realized by understanding the underlying deformation and failure mechanisms at high contact pressures. In this letter, for the first time, we report the microscopic evidence of amorphous B_6O that was produced by nanoindentation, indicating the failure of B_6O is associated with the shear amorphization.

B_6O powders were synthesized from the mixture of crystalline boron (β -B) and amorphous boron oxide (B_2O_3) by a solid-liquid reaction. The obtained B_6O powders were consolidated by the hot press technique at 2173 K, 60 MPa for 1h. A detailed synthesis procedure can be found in the previous report [14]. The relative density of bulk B_6O is ~97.5% (2.55 g/cm^3) of theoretical density (2.62 g/cm^3). A series of indentation tests were performed on smoothly polished B_6O surface at constant loading force (1 N) and loading rate (~14 mN/s) using a dynamic ultra-micro-hardness tester (Shimadzu W201S) equipped with a berkovich diamond indenter. The measured average hardness value was ~38 GPa. Raman spectra were collected using a Renishaw 1000 with the excitation wavelength of 633 nm of an argon laser source. The beam size of the laser spot is about 1 μm . As sintered B_6O TEM specimen was sliced from bulk and mechanically ground to ~150 μm . The surface of the thin

specimen was then dimpled to a thickness of about 20 μm and ion-beam milled to obtain electron transparency (Fischione 1010 Model). The cross sectional TEM specimens of the indented B_6O samples were prepared by lift-out technique using a focused ion beam milling (FIB) system (JEOL JIB-4600F) [15]. The cross-sectional indentation samples were subjected to a low voltage ion milling (i.e. 900 V) in a Fischione 1040 Nanomill system to remove the damage layers without altering surface chemistry before the TEM analysis. The microstructures of the as-prepared and deformed samples were characterized with a JEOL JEM-2100F transmission electron microscope equipped with Gatan imaging system for electron energy loss spectroscopy.

A typical TEM image of the as-sintered B_6O ceramic shows fine and tight grained microstructure (**Figure 1**). The grain size distribution of B_6O ranges from 100 nm to 2 μm with a mean size (std. dev) of about 400 (± 190) nm. Numerous stacking faults and twin bands in B_6O grains can be seen. The selected area electron diffraction (SAED) pattern (the inset of **Fig. 1**) reveals roughly equiaxed grains with random orientations separated by high-angle grain boundaries (GBs) (**Fig. 1**). High-resolution TEM observations (not shown here) display sharp GBs without any amorphous and crystalline interfacial phases.

To explore the possible phase transitions induced by the nanoindentation, Raman spectroscopy was employed to characterize the residual indentation impressions of B_6O . **Figure 2** shows the typical Raman spectra in the range of 200-2000 cm^{-1} acquired from the pristine and residual indented region of B_6O . The inserted SEM image shows the residual indentation at a load of 1 N. A number of characteristics Raman bands from the pristine B_6O reflect the complex atomic structure of B_6O . In low frequency region, the peak with uncertain origin is located at 262 cm^{-1} [16]. The bands at 373 cm^{-1} is associated with the motion of O-O pairs and the 499.5 cm^{-1} is related to the symmetric stretching of the O-O pairs [17]. The peak around 545 cm^{-1} is attributed to a motion of icosahedra boron atoms about oxygen atoms at

ends of the each chain [17, 18]. In high frequency region, the multiple bands at 734 cm^{-1} , 838 cm^{-1} , 882 cm^{-1} , 1017 cm^{-1} , 1089 cm^{-1} , 1134 cm^{-1} and 1178 cm^{-1} have assigned to intra-and inter-icosahedral vibrations of boron atoms [16-18]. A part from the vibration modes of B_6O , the additional peaks at 335 cm^{-1} , 411 cm^{-1} and 516 cm^{-1} might be associated with oxygen deficiency in B_6O and a weak band at 1285 cm^{-1} was attributed to unreacted boron oxide (B_2O_3) [18]. A broad peak between 600 to 700 cm^{-1} is the cause of strong fluorescence (F) by 633 nm (red) laser used in this study [17]. Compared with the Raman spectrum of the as-sintered B_6O , the spectrum obtained from the center of a residual impression shows the obvious changes in the Raman intensity and peak position (**Fig. 2**). The considerable peak broadening and red shift of the intra-and inter-icosahedral vibrations indicate that certain structure disorder associated with the B_{12} icosahedra is introduced by the nanoindentation experiment. However, no additional or disappearance of B_6O Raman bands can be found, which appears to be inconsistent with previously reported diamond anvil cell (DAC) experiment in which single crystal rhombohedral B_6O is observed to transform into an amorphous B_2O_3 and a glassy boron phase under quasi-static pressure of 90 GPa [19]. Since the nanoindentation contact pressure of $30\text{-}40\text{ GPa}$ is significantly lower than that of the DAC experiment, it is apparently insufficient to cause the global phase transition of B_6O and, instead, only produce local structural changes accompanying with the inelastic deformation driven by shear components.

In order to verify the structural transformation caused by nanoindentation, focused ion beam (FIB) milling was employed for the preparation of cross-sectional TEM specimens from the residual indentation of B_6O . The detailed procedure for the lift-out technique using FIB milling has been described in our previous report [15]. The low magnification bright-field and dark-field scanning transmission electron microscopy (STEM) images of B_6O beneath the indenter region show several crack regions and deformation shear bands with

variations in contrast, which are indicated with black and white arrow heads (**Figs. 3(a)** and **(b)**). Moreover, a number of dislocations, which are rarely seen in the as-prepared samples, appear in the vicinity of the deformation bands and micro-cracks, suggesting that the conventional dislocation plasticity is involved into the indentation deformation besides microcracks and shear bands. The deformation shear bands usually have a width of ~1-3 nm and length of 200-300 nm. High-resolution STEM reveals the loss of lattice fringes in the bands (**Fig. 3(c)**). The fast Fourier transform (FFT) pattern taken from the band shows a diffused halo without any crystalline diffraction spots, which confirms the amorphous nature of the shear band (Inset B). By contrast, FFT patterns taken from both sides of the band reveals the parent crystal structure of $[10\bar{1}1]$ rhombohedral B_6O (Inset A and C) (**Fig. 3(c)**). The angular mismatch between the lattice fringes from both sides of the amorphous band is smaller than 1° . This observation suggests that mode-I-type displacements do not play a marked role in the formation of the amorphous bands, which is consistent with the fact that the width of the amorphous zone does not change substantially along the length of the zone. Instead, the lattice shift of the two-side crystals along the narrow zone indicates that the amorphous band is produced by localized mode II or mode III shear instabilities. All the STEM images were taken by tilting to nearly perfect alignment on both sides of amorphous band, the possibility of diffused grain boundaries and local melting into amorphous phase can be ruled out. Chemical analysis of the amorphous and crystalline B_6O regions was carried out using STEM electron energy loss spectroscopy (STEM-EELS). No detectable compositional difference in the boron-to-oxygen ratios between the two regions can be found, indicating that the amorphization does not result from the chemical decomposition of B_6O or pressure-induced chemical reaction (**Fig. 3(d)**). Thus, we suggest that the observed nanoscale amorphous shear bands occurred as solid state phase transformation during nanoindentation deformation, similar to those in B_4C [20-22].

Shear induced amorphization has been observed in many inorganic materials [23-26]. However the underlying mechanisms remain to be poorly known. **Fig. 4(a)** is a BF-STEM image that shows dislocations loops taken from one end of the amorphous band. The dislocation loops are indicated by a black T and inverted $\perp$ (**Fig. 4(a)**). High lattice disorder can be observed in the regions of the dislocation loops, indicating that the lattice collapse of the crystals lattice is related to the dislocations accumulation during shear sliding. The Burgers vectors of these dislocations fall on crystallographic plane $(0\bar{1}11)$. The preferential amorphization plane is probably originated from the large elastic anisotropy and the large bonding length difference among B-B (0.14 nm), B-O (0.18 nm) and O-O (~ 0.3 nm) in B_6O [7, 27-28]. Since the $(0\bar{1}11)$ crystal plane contains relatively weak O-O bonds, it may be easy to slide and the breaking of the O-O chains may lead to the amorphization of B_6O , as shown in the schematic diagram (**Fig. 4(b)**).

Inevitable micro-scale flaws, such as micro-cracks and inclusions, introduced by sintering, usually lead to ceramics failure in a brittle manner without any plasticity at a low applied stress. However, under extreme loading conditions (such shock loading [20, 29], small volume and confined deformation (indentation [21, 15] and diamond anvil cells [10])), the cracking can be completely suppressed and the materials can exhibit their intrinsic deformation behavior by either dislocation plasticity or phase transition. For the super-hard materials, such as diamond, B_4C and BO_6 , the strong covalent bonds may lead to very high Peierls stresses for dislocation motion at low temperatures. Thus, those materials cannot plastically deform by pure dislocations even the cracking is suppressed. If there is a relatively weak crystallographic plane for shearing, it may cooperatively slip with or without the assistance of dislocations. This kind of rigid slip often results in the local shear amorphization because of the break of local order and translational symmetry [22].

B₆O has ultrahigh hardness but very low fracture toughness because of the easy formation and propagation of cracks. Traditionally, the brittleness of the high-strength ceramics is often attributed to the intrinsic fragility of chemical bonds that are strong but not flexible to tolerate deformation. However, the detailed [experimental](#) failure process of these chemical bonds is less known. The formation of nano-sized amorphous bands in B₆O, subjected to shearing, offers new insights of the brittle failure of the super-hard materials at a much lower stress than their theoretical strength. The brittleness is not from the direct failure of the rigid bonds under model I-type normal stresses and, instead, caused by the shear induced structure instability. Shear deformation usually leads to plastic strains and hence enhances materials ductility. However, in highly isotropic materials, the preferential sliding along weakly bonded atomic planes may result in local structure collapse and failure. This type of shear induced amorphization and materials failure is probably a popular phenomenon in high-strength materials with significant structural and elastic anisotropy.

Acknowledgments

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Figure list

Figure 1. A typical TEM image of polycrystalline B₆O synthesized at 60 MPa and 2173 K for 1h. The SAED pattern of B₆O is inserted to the TEM image.

Figure 2. Representative Raman spectra of B_6O (a) pristine surface and (b) residual indentation obtained using an argon ion laser with excitation wavelength of 633 nm. Inset SEM image shows the Berkovich indented impression at a load of 1 N.

Figure 3. (a) Bright field (BF) STEM and (b) Dark field (DF) STEM images showing several cracks (black arrow head) and shear bands (white arrow head) beneath the indenter. (c) zoom-in BF-STEM image of the amorphous band along the $[10\bar{1}1]$ direction of crystalline B₆O (Inset FFT pattern A). The loss of lattice fringes in the band indicates the B₆O amorphization (Inset FFT pattern B). (d) STEM-EELS spectra obtained from (A) crystalline lattice and (B) amorphous B₆O.

Figure 4. (a) BF-STEM image of B_6O shows the dislocations loops at the end of the amorphous shear band. (b) A schematic of localized softening of amorphization B_6O along the sliding plane $(0\bar{1}11)$. The blue color is boron and red color is oxygen atoms.