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Observations of grain boundary chemistry variations in a boron carbide processed with oxide additives



Kristopher D. Behler^{a,b,*}, Christopher J. Marvel^c, Jerry C. LaSalvia^a, Scott D. Walck^{a,b}, Martin P. Harmer^c

^a U.S. Army Research Laboratory, RDRL-WMM-E, Aberdeen Proving Ground, MD 21005-5069, United States

^b Survice Engineering, 4695 Millennium Dr., Belcamp, MD 21017, United States

^c Lehigh University, Department of Materials Science and Engineering, Bethlehem, PA 18015, United States

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ABSTRACT

Analytical electron microscopy was used to examine the grain boundary chemistry in boron carbide containing Al-O-rich phases at triple junctions. In this study, SiO₂, Al₂O₃, and B₂O₃ additives were used to synthesize an aluminoborosilicate glass on the grain boundaries with the long-term goal to enhance fracture resistance. Nanolayer films were not observed using high-angle annular dark field imaging; however, energy-dispersive spectroscopy quantification revealed grain boundaries with varying excess of Si and Al. Overall, it was concluded variations in grain boundary chemistry depend upon the intrinsic grain boundary character and spatial heterogeneity of the oxide additives.

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Boron carbide is a nonstoichiometric ceramic compound whose phase stability ranges between 8.8 and 20 at.% C [1–4]. Its crystal structure comprises of two distinct structural units, a 12-atom icosahedra and a 3-atom linear chain that are arranged in a rhombohedral crystal lattice. Combined with strong covalent bonding, boron carbide possesses a low density and high shear strength; properties ideal for armor and wear applications [1–8]. Unfortunately, the covalent bonding attributes to a low intrinsic fracture resistance thereby limiting the performance and use of boron carbide [7,9–12].

Several microstructural engineering approaches have been developed and applied to improve the fracture resistance of ceramics through extrinsic mechanisms, such as phase transformations, microcracking, crack-deflection, and crack-bridging, which effectively reduce the stress-intensity associated with the far-field applied load [13–15]. Silicon nitride (Si₃N₄) ceramics, an important class of structural ceramics, have been developed with high fracture toughness values (>6 MPa·m^{1/2}) based on crack-deflection and crack-bridging mechanisms [16–17]. The key microstructural features for these tough Si₃N₄ ceramics are elongated grains and liquid-like nanolayer films (previously referred to as intergranular films (IGFs) within grain boundaries) [18–19]. These nanolayer films weaken grain boundaries enabling intergranular fracture morphology, while the elongated grains serve to

deflect the crack-tip out of the preferred crack path (i.e. Mode I) and bridge crack surfaces. The presence of the nanolayer films are key to these mechanisms, since transgranular fracture morphology would otherwise be favored.

Since the first lattice image observations of grain boundaries in Si₃N₄ by Clarke [20], significant advances have been made in understanding the effects of the chemistry and structure of nanolayer films on electrical, mechanical, and thermal properties of ceramics [21–23]. These observations of nanolayer films have been strongly supported by the emergence of electron microscopes with sub-Angstrom spatial resolution and the development of thermodynamics and force-balance models that predict their stability and thicknesses [24–27]. Based on the concept of grain boundary or interfacial complexions, nanolayer films are one type of interfacial equilibrium state and they have been observed in numerous ceramic-ceramic, metal-metal, and ceramic-metal systems [24,28–32]. The term interfacial complexion has been put forth as a word to describe the equilibrium state of an interface and can describe grain boundaries, phase boundaries, and surfaces. One important difference between bulk phases and interfacial complexions is that they cannot be stable without the abutting phases on either side of the interface [28–32]. However, like bulk phases, interfacial complexions exhibit first-order transitions from one complexion type to another that depend on critical values for thermodynamic parameters. In addition to nanolayer films, other types of interfacial complexions have been observed in a variety of material systems [28–32]. More importantly, their profound influence on a variety of material phenomena

* Corresponding author.

E-mail address: kristopher.d.behler.ctr@mail.mil (K.D. Behler).

including fracture, densification, grain growth, electrical conductivity, and others are beginning to be recognized.

To date, there have been no reported observations of nanolayer adsorbate complexions in boron carbide. Past studies on boron carbide hot-pressed with sintering additives have shown either sharp clean grain boundaries or thick grain boundary wetting films [6,33–36]. Other grain boundary complexions, such as monolayer and bilayer types [29], may exist but have not been reported. In this paper, results from analytical electron microscopy (AEM) techniques that were used to characterize the grain boundaries in a boron carbide hot-pressed with alumina (Al_2O_3), silica (SiO_2), and boron oxide (B_2O_3) additives are reported. These oxide additives are constituents for an aluminoborosilicate glass which promotes densification and the possible creation of liquid-like nanolayer grain boundary films. The intention of the current work is to elucidate the effect of these oxide additives on the structure and chemistry of grain boundaries of boron carbide. The insight gained may eventually lead to the development of boron carbide ceramics with engineered grain/phase boundaries that impart improved fracture resistance and quasi-plasticity [6–7].

Boron carbide powder was purchased from H.C. Starck GmbH & Co (Grade HS). As-received powder was densified as described below, and additional powder was acoustically mixed (LABRAM) with approximately 5 vol.% oxide additives consisting of Al_2O_3 (SM8, Baikowski), SiO_2 (from tetraethoxysilane, Alfa Aesar), and B_2O_3 (from H_3BO_3). Based on earlier work [6], the additive composition (71.5 wt.% Al_2O_3 , 21.4 wt.% SiO_2 , 7.1 wt.% B_2O_3) was chosen to produce a refractory aluminoborosilicate glass that can withstand the high temperature required to densify boron carbide. Al_2O_3 is an effective densification aide for boron carbide [37], while SiO_2 a strong glass former and the basis for liquid-like nanolayer films in structural ceramics such as silicon carbide (SiC) and Si_3N_4 [18–20,24]. The addition of B_2O_3 (native oxide of boron carbide) was included in an attempt to enhance the wettability of the intended aluminoborosilicate glass and thereby improve its distribution throughout the microstructure. Near full density (>95% TD) for the as-received and fully dense doped powders was achieved in a laboratory hot-press (Oxy-Gon Industries) at 2000 °C and 1900 °C, respectively for 3 h with a uniaxial pressure of 17 MPa.

After hot-pressing, the sample was removed from the die, cut, and polished for phase analysis and microstructural characterization. X-ray diffraction (XRD) was conducted using a PANalytical X'Pert MRD PW3040/60. AEM specimens were prepared using either a FEI Nova NanoLab Focused-Ion Beam (FIB) or a FEI Scios FIB. High-angle annular dark field (HAADF) imaging, low-angle annular dark field (LAADF) imaging, and energy dispersive spectroscopy (EDS) were conducted using a JEM-ARM200CF. The angular ranges of the HAADF and LAADF detectors were 54–220 mrad and 24–96 mrad, respectively. The JEM-ARM200CF is equipped with a CEOS ASCOR 4th order spherical-aberration corrector and a 100 mm² silicon drift EDS detector. EDS maps were constructed after subtracting the background in each elemental peak. Grain boundary compositions were measured based on the technique described by Keast and Williams [38–39]. Three rectangular regions were probed, one on the grain boundary and one each in the abutting grains, and the difference between the grain boundary and average matrix compositions were calculated. Based on the Cliff-Lorimer equation [40], the number of *i*th element atoms per unit grain boundary area (atoms/cm²) \bar{n}_i^{gb} is given by $\bar{n}_i^{gb} = 4k_{iB}n_{B4C}W(AW_B/AW_i)[(I_i/I_B)^{gb} - (\bar{I}_i/I_B)^g]$ where k_{iB} is the Cliff-Lorimer factor for the *i*th element relative to B (major constituent of boron carbide), n_{B4C} is the atomic number density for boron carbide (2.75×10^{22} atoms/cm³), W is the width (cm) of the rectangular region from which X-rays were collected, AW is atomic weight, I is the peak intensity (FWHM minus background), $(I_i/I_B)^{gb}$ is the relative X-ray peak intensity from the grain boundary region, and $(\bar{I}_i/I_B)^g$ is the averaged relative X-ray peak intensity from the abutting grains. The calculated k_{AlB} and k_{SiB} used in this analysis are 0.11 and 0.09, respectively.

The microstructures of the hot-pressed boron carbide samples are shown in Fig. 1. The boron carbide grains in the as-received (Fig. 1A) and doped (Fig. 1B) conditions were equiaxed with average grain sizes of $1.8 \pm 0.3 \mu\text{m}$ and $2.2 \pm 0.4 \mu\text{m}$, respectively. In the doped powder, second phases were located predominately at grain boundary triple junctions. The phases were qualitatively identified as Al_2O_3 , Al—Si—O—rich, or WC by EDS. XRD results showed only peaks corresponding to boron carbide and Al_2O_3 . No WC or Al—Si—O phase was detected. The morphology of the second phases at triple junctions indicated partial wetting, which suggested the possible presence of multi-layer adsorbate complexion types.

Considering the possible wetting along the grain boundaries seen in Fig. 1B, the grain boundaries nearest to second phases were investigated. Fig. 2A shows a HAADF image of a second phase particle at a triple junction. In this region of interest, there are two phase boundaries between the second phase and boron carbide, and a boron carbide grain boundary horizontally across the image. HAADF intensity scales with atomic number; thus, the brighter regions in the second phase and along the grain boundary indicate the presence of a higher atomic number element(s) relative to the average atomic number of boron carbide. Figs. 2B–2E are EDS $K\alpha$ maps for Al, O, Si, and Ca respectively. Ca is an impurity element associated with Al_2O_3 . The second phase was determined to be Al- and O-rich, consistent with SEM EDS observations. Furthermore, the presence of excess Si and Ca on the phase boundaries was clear, but only an excess of Si was obvious along the boron carbide grain boundary. Both the lower phase boundary and boron carbide grain boundary are inclined, most evident by the diffuseness of the Si and Ca $K\alpha$ maps.

The structures of the grain and phase boundaries were investigated with STEM imaging. Fig. 3A shows a triple point with no apparent second phase and three grain boundaries, labeled as GB1, GB2, and GB3. The specimen was tilted to align the basal (c-plane) of the lower-left grain normal with respect to the beam. GB1 and GB2 are tilted relative to the beam and GB3 is in a near edge-on condition. The LAADF image in Fig. 3A clearly shows segregation of higher atomic number elements to GB3. The boxed region in Fig. 3A is further magnified showing the interface more clearly in Fig. 3B. Despite the alignment of the grain boundary relative to the beam, no apparent nanolayer film was observed, even though the low magnification image indicates the possible presence of a film. Furthermore, it was observed that the grain boundary is faceted with apparent step sizes varying from 2 to 4 boron icosahedra. Fig. 3C shows an Al—O rich phase boundary similar to the example shown in Fig. 2. The boxed region in Fig. 3C is magnified in Fig. 3D with the grain on the left oriented to the basal plane. An obvious interfacial nanolayer film was not observed even though the EDS analysis indicated an excess of Si and Ca. The phase boundary is atomistically flat with no facets in the plane of boron icosahedra.

Based on the qualitative examination of approximately 100 grain boundaries (three STEM specimens) under HAADF conditions, the general observation was the lack of clear evidence for nanolayer films at grain boundaries. However, the observation of Si and Al segregation shown in Fig. 2 suggests that the addition of Al_2O_3 , SiO_2 , and B_2O_3 affected grain boundary chemistry. Therefore, the chemistries of many grain boundaries in the as-received and doped boron carbides were directly compared and the grain boundary excess of Si and Al are compared in Fig. 4. The number of monolayers (i.e. monolayer = $n_{B4C}^{2/3}$), as shown on the y-axis, was chosen to better convey the physical amounts of segregated atoms on the grain boundaries as compared to an area density, but it should be mentioned, the number of monolayers in this case does not physically indicate if there is a monolayer, bilayer, trilayer, etc. Due to assumptions in the analysis, primarily that the grain boundary planes of each boundary are unknown, the relative concentrations of segregant on each boundary should be compared without much physical understanding of the grain boundary structure. Nevertheless, a positive value indicates an excess on the grain boundary, and a negative value indicates a deficiency where there are fewer atoms on the grain boundary compared to the grain interiors.

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