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Recent Developments of ζ-factor Microanalysis and Its Application to Armor Ceramics

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This work outlines several recent developments and applications of ζ-factor microanalysis, a quantitative (scanning) transmission electron microscopy ((S)TEM) X-ray energy dispersive spectroscopy (XEDS) method that corrects for X-ray absorption, for compositionally characterizing armor-grade boron-based ceramics down to atomic-length scales [1].

Boron-based ceramics, in particular boron carbide, are used as armor ceramics because they exhibit low density (~2.52 g/cm^3) and high hardness (~40 GPa) [2]. Density and hardness are important properties because they reduce weight and maximize resistance to high-rate ballistic impacts, respectively [3]. Recent attempts to improve ballistic performance have been to strategically weaken grain boundaries to promote intergranular fracture, rather than transgranular fracture, thus increasing crack lengths and thereby improving fracture resistance [4]. Therefore, there is a need to accurately characterize boron carbide on fine length-scales to best understand, validate, and leverage interfacial process-structure-property relationships. Unfortunately, reliable compositional analysis of boron carbide, on any length-scale, is challenging. Conventional methods to analyze boron carbide (e.g. X-ray diffraction, Raman spectroscopy, combustion gas analysis) only reveal overall compositions without local composition fluctuations (e.g. at grain boundaries). Higher resolution analytical techniques in STEM (e.g. XEDS or electron energy loss spectroscopy (EELS)) are rather limited by X-ray absorption for XEDS, and sensitivity of background subtraction and the difficulties of signal detection of certain rare-earth elements for EELS which are common dopants used to improve performance of armor-grade ceramics. Overall, there was a need to develop a technique that can efficiently and accurately determine boron carbide bulk stoichiometry and grain boundary compositions.

This work extended ζ-factor microanalysis to analyze boron carbide bulk stoichiometry and grain boundary composition. A collection of K-family ζ-factors were determined using a NIST SRM-2063a thin film [5]. B K and C K ζ-factors were independently determined using an extrapolation technique from wedged thin specimens of SiB_6 and SiC, respectively. Figure 1a shows the ζ-factors generated during this work where the open diamonds were directly determined from SiB_6 and SiC, the open circles were determined through the glass standard, and the closed circles were estimated from the determined ζ-factors. Figure 1b compares measurements of B concentration in SiB_6 as a function of the specimen thickness with and without the absorption correction. The dashed line represents the nominal B concentration of stoichiometric SiB_6. Upon correcting for absorption, the constant B concentration (i.e. independence of sample thickness) was considered validation that ζ-factor microanalysis can accurately analyze boron-rich materials. Figure 1c shows the absorption factors that were applied for absorption corrections, exceeding 250% at sample thicknesses above 100 nm. In addition, three bulk boron carbide

specimens with different stoichiometries were analyzed and the measured compositions were validated with combustion gas measurements of the same bulk materials. Raster scan methods to determine grain boundary composition using ζ-factor results were also extended based on prior techniques [6,7]. Overall, it was concluded that ζ-factor quantification is a viable method to determine boron carbide stoichiometry and grain boundary composition.

An additional application, in which ζ-factor quantification was central to the experimental capability, is to determine maximum Si solubility in boron carbide and average interfacial Si excess coverages as a function of bulk Si concentration within the polycrystalline diffusion zone of a SiB_6/B_4C diffusion couple heat treated at 1650 °C for 24 hours. The diffusion couple was used to determine maximum Si solubility in the boron carbide lattice and the consequential changes to B/C stoichiometry and Si segregation behavior. Furthermore, if sufficient Si segregation was to occur, it was hypothesized that thick nanolayer complexions would form [8], thereby weakening grain boundaries and improving fracture resistance. Figure 2a shows a backscatter electron micrograph of the diffusion couple and the locations where thin specimens were extracted for ζ-factor quantification. Figures 2b-d shows high-angle annular dark field STEM images where it was observed that the grain boundary structure at different points in the diffusion zone did not undergo much change, suggesting that a thick nanolayer complexion is not stable under these given processing conditions. However, as shown in Figure 2e, the average grain boundary composition (i.e. excess Si coverage in atoms/nm^2) was measured to increase with increasing bulk Si concentration in the diffusion zone, thus suggesting that while a structural complexion transition did not occur, there was indeed a wide variability in grain boundary composition. This result supports the notion that grain boundaries could be relatively weaker with increasing Si coverage. Overall, the maximum Si solubility in the matrix was measured as 1.7 at.%, corresponding with a 5.6 B/C ratio, and the maximum Si excess coverage was 8.7 atoms/nm^2. Notably, considering the nearly constant increase of Si excess coverage against Si concentration in the bulk, it was determined that the grain boundary segregation behavior agrees with the Gibbsian absorption definition where a higher bulk solubility leads to an increase of grain boundary segregation [9].

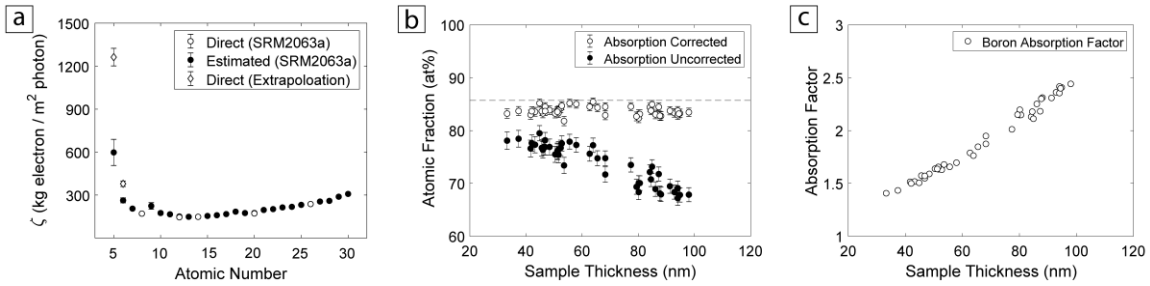

Figure 1. Summary of (a) ζ-factors used throughout this study, (b) B concentration vs sample thickness measured from a SiB6 standard which was used as validation, and (c) a summary of the associated absorption correction factors applied to the B K-line X-rays where a 250% correction was applied at a sample thickness of 100 nm.

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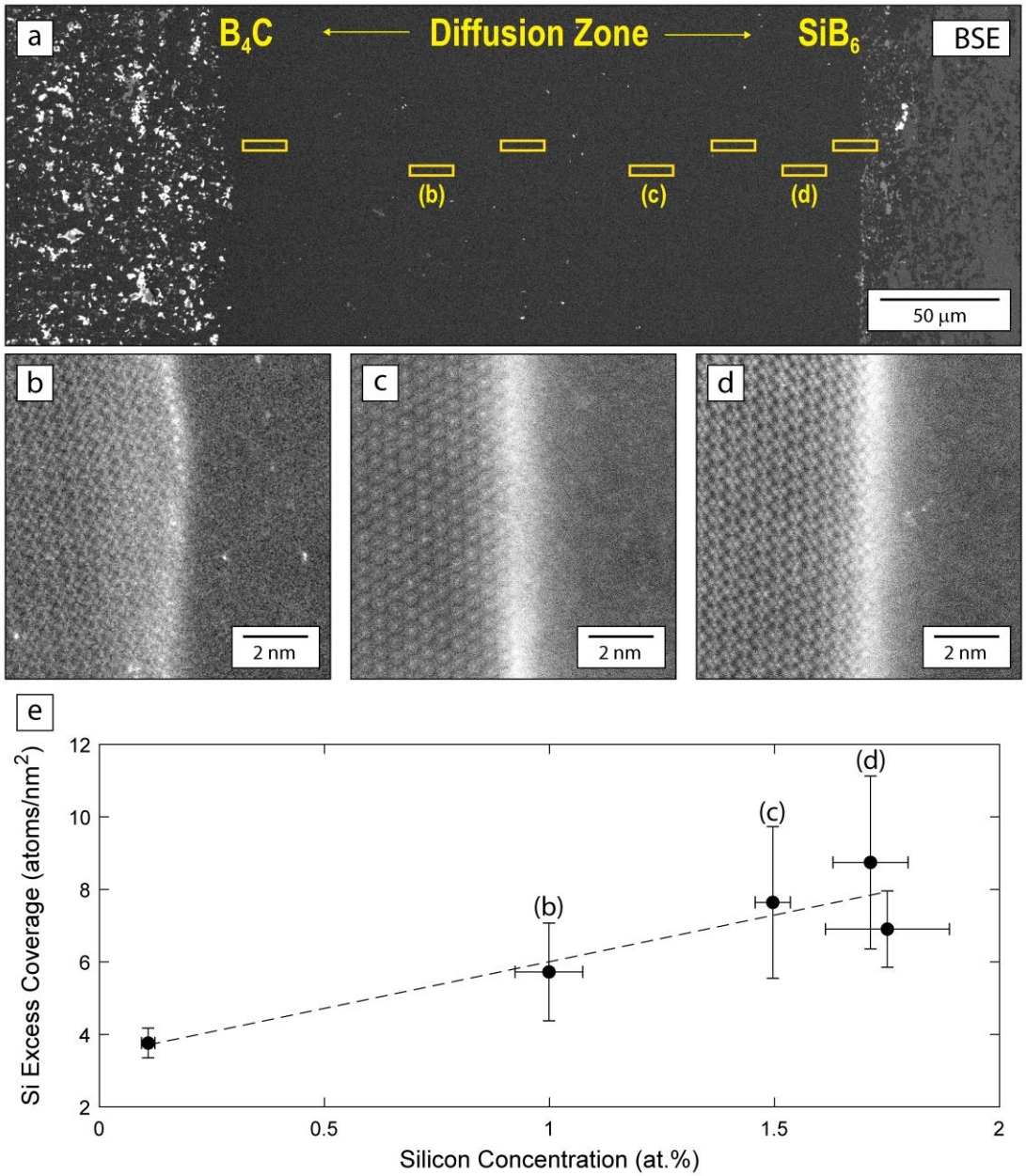

Figure 2. Summary of analytical results from the (a) B4C:SiB6 diffusion couple where multiple thin specimens (shown in yellow) were extracted for ζ-microanalysis , (b-d) high-angle annular dark field micrographs showing minimal differences in grain boundary structure from different regions of the diffusion zone, and (e) grain boundary segregation dependence of Si concentration in the bulk boron carbide lattice.

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