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ζ–Factor Development and Quantification of a Boron Carbide and Silicon Hexaboride Diffusion Couple

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Boron-rich ceramics have been investigated as candidate materials for armor applications because of their high hardness and low density [1]. However, these materials are susceptible to amorphization under stress and exhibit low fracture resistance [2]. One strategy to reduce amorphization and improve fracture resistance is to incorporate Si-rich additives during processing. This strategy has been shown to be successful as dissolved Si in the B_4C lattice mitigates amorphization [3], and Si-rich grain boundary complexions could alter bulk B_4C fracture mechanisms similar to nanolayer complexions in silicon nitride [4]. While material properties are improved with Si-rich additives, there has been historically less progress to accurately quantify Si dissolution or grain boundary chemistry in boron-rich ceramics, especially using conventional analytical techniques such as X-ray energy dispersive spectroscopy (XEDS) or electron energy loss spectroscopy (EELS). Therefore, an analytical capability that can help link material performance to material chemistry in boron-based materials is needed. This work extended the ζ–factor approach to develop a new capability to analyze boron-rich ceramics [5].

A diffusion couple with boron carbide (B_4C) and silicon hexaboride (SiB_6) was fabricated to produce Si-doped B_4C, to measure the maximum Si solubility in the B_4C lattice, and to quantify excess segregation levels of Si-doped B_4C grain boundaries. Thin specimens were fabricated using a FEI Scios focused ion beam and XEDS analysis was completed using a JEOL ARM-200CF instrument equipped with a JEOL large-angle silicon drift detector. ζ–factors of boron and carbon K_α lines were determined from high purity borides and carbides, respectively, and the ζ–factors of other remaining K_α lines were determined from a NIST 2063a standard reference glass thin film. Spectrum images were acquired and grain boundary excess values were determined using a raster scan technique [6].

Figure 1 summarizes a spectrum image of a B_4C / boron suboxide (B_6O) interface. The B_6O was a product of oxygen impurities during processing, but it was a convenient region of the specimen to validate the ζ–factor method by comparing two different boron-rich compounds. Overall, the B_4C/B_6O interface is clearly resolvable and multiple second phases were located near the boundary. Furthermore, the primary second phase exhibited an internal two-phase mixture consisting of Si-O-rich and Al-Mg-O-rich regions and Mg and Al segregation to the B_4C and B_6O phase boundaries. SiB_6 and pure Si secondary phases were also observed. The boron concentrations of the B_4C and B_6O were 87.3 ± 2.0 at.% and 88.4 ± 1.3 at.% B, respectively. In addition, the Si concentration was measured to be 1.5 ± 0.1 at.%, which was less than solubility limits found in the literature. All error values are reported as 95% certainty (2σ).

Grain boundary excess planar densities in B_4C were quantified to determine the variability of grain boundary segregation. Figure 2 compares two grain boundaries: one boundary exhibits minimal segregation (a) and the other exhibits strong segregation (b). The excess planar densities of Si and Al in

the boundary exhibiting strong segregation were 4.6 ± 3.2 and -0.02 ± 0.15 atoms/Å^2, respectively, and the Si and Al excess planar densities in the boundary exhibiting minimal segregation were 0.86 ± 3.6 and 0.03 ± 0.2 atoms/Å^2, respectively. In summary, the average excess planar densities were quantified and can be accurately measured using this methodology.

Overall, this ζ–factor analytical framework to quantify boron-rich ceramics will provide a required insight to accelerate the materials design process. It can produce chemistry data with high accuracy and statistical confidence, and in combination with multiple grain boundary measurements, it can predict a grain boundary chemistry distribution for a given microstructure. Furthermore, these techniques can be utilized to investigate lattice and grain boundary concentrations in other light-element materials.

References:
[1] V. Domnich *et al*, Journal of the American Ceramic Society **94** (2011) p. 3605–3628.
[2] G. Subhash *et al*, Scripta Materializ **123** (2016) p. 158–162.
[3] J.E. Proctor *et al*, Journal of Physics Condensed Matter **27** (2014) p. 015401.
[4] K.D. Behler *et al*, Scripta Materialia **142** (2018) p. 106–110.
[5] M. Watanabe, D.B. Williams, Journal of Microscopy **221** (2006) p. 89–109.
[6] V.J. Keast, D.B. Williams, Journal of Microscopy **199** (2000) p. 45–55.

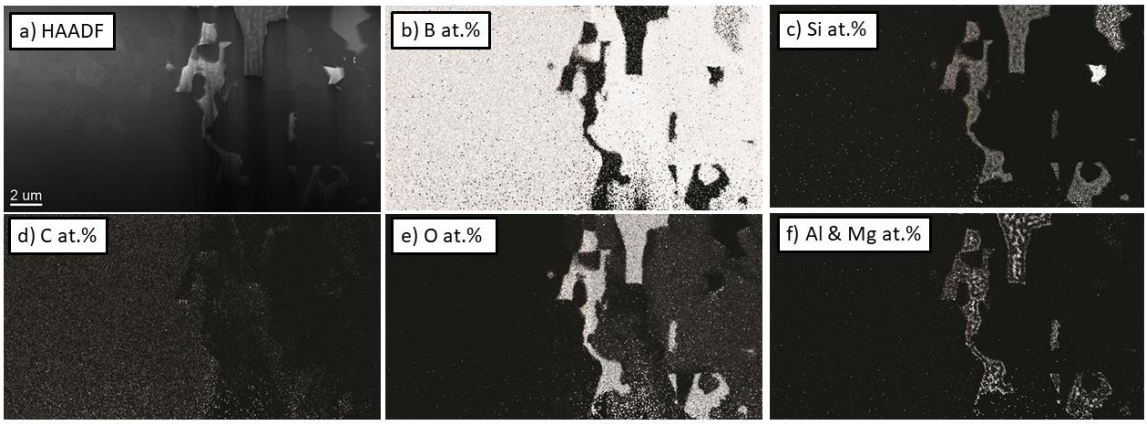

Figure 1. Figure 1a shows a reference high-angle annular dark field reference image, and Figures 1b-f show the boron, silicon, carbon, oxygen, aluminum, and magnesium composition maps.

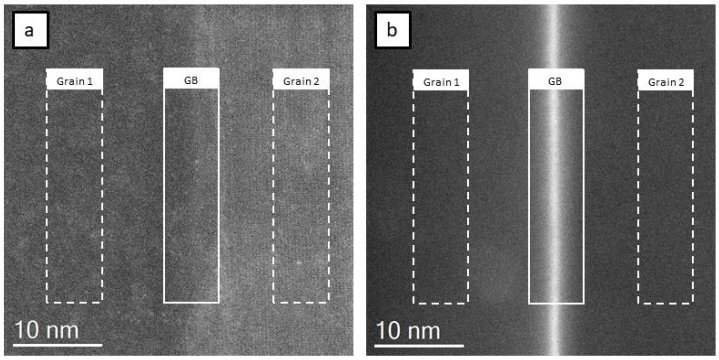

Figure 2. Figures 2a and 2b show the grain boundaries that exhibited minimal and strong segregation. Each image is a high-angle annular dark field image and the three boxes visualize the raster scan method.

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