Effects of silicon additives on the microstructure of boron carbide ceramics

Lowry Brooks
Mentored by Dr. Jerry LaSalvia and Dr. Kristopher Behler

Introduction

Sintered ceramics are compounds of grains of material that have been densified through heat. These compounds have a large range of uses, from basic pottery, to ceramic armors that are used by the military. In the body armor aspect, an important ceramic used is boron carbide (B_4C), due to the fact that B_4C is not only one of the hardest ceramics, but also one of the lightest (lowest density) (Rehman, Ji, Khan, Fu, & Zhang, 2014). These conditions allow the armor to protect the wearer without weighing them down too much. However, due to boron carbide's high melting point (2450 °C) and strong covalent bonds, ceramics made of pure B_4C tend to be unable to achieve full density and to be brittle (Behler et al., 2016). A solution to this problem is mixing the B_4C powder with sintering additives. Sintering additives are materials that are added to the B_4C before the ceramic is fired. These additives can help decrease sintering temperature without excessively harming the overall hardness of the ceramic (Rehman et al., 2014). In a previous study done by Aberdeen Research Laboratories (Behler et al., 2016) they tested the effect of mullite ($3Al_2O_3{:}2SiO_2$) additives on B_4C ceramics. While examining the resulting ceramic, they found that while the alumina was forming at the intersection of three-grain boundaries, the silicon segregated to the B_4C grain boundaries. To develop further upon these findings, this experiment focuses on the effects varying amounts of silicon additives have on the densification, hardness, and microstructure of B_4C ceramics.

Materials and Methods

Boron carbide powders (H.C. Starck HS Grade) were combined with tetraethyl orthosilicate and acoustically mixed in ethanol for 15 minutes. The powders were dried in a glove box at 50 °C for 24 hours to create mixtures of 1.5 – 3.0 atomic percent (at%) silicon (Behler, 2016). Five grams of powder was hand crushed, loaded into a graphite die assembly, and prepressed at 44 MPa. The samples were heated and compressed using a bench-top hot-press at 2000 °C and 2000 lbf for 3 hours under an argon atmosphere to produce 1" ceramic disks. During hot pressing, the densification of each sample was measured by recording the hot press ram displacement using a linear variable displacement transducer. The thermal expansion of the assembly was separately recorded, and then subtracted from the displacement of the powder to create a densification curve for each sample. After hot pressing, the density of these disks was measured using the Archimedes method. A small slice of the ceramic was cut, mounted in epoxy, and polished, so that 2 kg indents could be made using a Knoop hardness tester. Before indents where made the samples where checked for pullout or excessive porosity using a scanning electron microscope (SEM) (Figure 1). These indents can be used to evaluate the hardness of the ceramic (ASTM C1326-13). Hardness values were calculated using the equation.

$$HK = 0.014229\left(\frac{F}{d^2}\right)$$

where F is the force applied in newtons and d is the length of the indent. Finally, the samples underwent X-ray diffraction to evaluate the composition of each ceramic as well as to calculate the theoretical density of the ceramic, which was compared to the actual density to provide a percentage theoretical density yield.

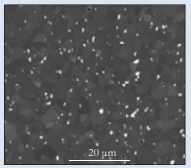


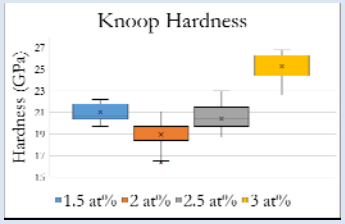
Figure 1: Image of the 3.0 at% Si sample obtained by SEM.

Results

The boron carbide with 3.0 at% silicon had a much higher Knoop hardness than the other samples (Graph 1), averaging 25.3 Gigapascals (GPa) for the 15 indents made, with 1.5 at% having the second highest hardness at 21.0 GPa, 2.5 at% following at 20.4 GPa, and 2.0 at% having the lowest hardness at 19.0 GPa (Table 1). With regards to density, 3.0 at% also was the highest, followed by 2.0 at%, 2.5 at%, and then 1.5 at%. However, as the concentration of silicon was increased the percentage theoretical density yield increased (Table 1). The X-ray diffraction data showed that the increase in silicon at% increased the amount of silicon carbide present in the sample until 3 at% silicon was reached where the amount of silicon carbide present in the sample dropped to values just slightly above the 1.5 at% sample.

Sample	Average Hardness (GPa)	Density (g/cm^3)	Theoretical Density Yield
1.5 at% Si	21.0	2.356	95.4%
2.0 at% Si	19.0	2.415	97.9%
2.5 at% Si	20.4	2.380	97.9%
3.0 at% Si	25.3	2.501	98.6%

Table 1: The table above shows the density, hardness, and theoretical density achieved for each sample.



Graph 1: The graph to the left represents the distribution of hardness values for the 15 indents measured for each sample.

Conclusions

The goal of this experiment was to study the effect of silicon additives on the microstructure and hardness of boron carbide ceramics. Each sample except the 2 at% was able to exceed the hardness value of commercial B_4C (19.8 GPa) (Vargas-Gonzalez, Speyer, & Campbell, 2010) with the 3 at% exceeding the hardness of the other samples by a significant amount, based on a two sample *t*-test. From the percentage theoretical density, we can see that as the silicon concentration is increased, the theoretical density achieved increases as well, with the 3 at% almost reaching full densification (Table 1). The x-ray diffraction data showed that the addition of silicon increased the amount silicon carbide in each sample until 3 at% was reached. At this time, the silicon carbide amount decreased and no other silicon compounds were detected. A possible cause for this is that the silicon could have been forming in-between the grain boundaries of the boron carbide and thus could not be picked up via x-ray diffraction. This would also account for the high hardness of the 3 at% silicon. The hardness and densification values indicate that 3 at% silicon additives would be a strong candidate for further study and possible future development into military grade armors.

Further experiments should be done on the 3 at% ceramic to confirm that the silicon is forming in-between the grain boundaries. Furthermore, since we have not seen a decrease in hardness values as silicon concentration surpassed 2 at%, further studies should be conducted to determine how much silicon can be added without reducing hardness, since an increase in silicon would result in an increase in theoretical density yield for the resulting ceramic.

References

ASTM C1326-13, Standard Test Method for Knoop Indentation Hardness of Advanced Ceramics, ASTM International, West Conshohocken, PA, 2013, DOI: 10.1520/C1326, www.astm.org

Behler, K. D., LaSalvia, J. C., Shanholtz, E. R., Golt, M. C., Walck, S., & Kuwelkar, K. A. (2016). Effect of Al_2O_3 on the Densification and Microstructure of B_4C. *Advances in Ceramic Armor, Biocerамics, and Porous Materials: Ceramic Engineering and Science Proceedings Volume 37*, (4), 21.

Rehman, S. S., Ji, W., Khan, S. A., Fu, Z., & Zhang, F. (2014). Microstructure and mechanical properties of B_4C densified by spark plasma sintering with Si as a sintering aid. *Ceramics International, 41*(1), 1903-1906.

Vargas-Gonzalez, L., Speyer, R. F., & Campbell, J. (2010). Flexural strength, fracture toughness, and hardness of silicon carbide and boron carbide armor ceramics. *International Journal of Applied Ceramic Technology, 7*(5), 643-651.

Acknowledgments

I would like to thank Dr. Behler and Dr. LaSalvia for guiding me through this project. As well as everyone at ARL for helping me during the year.