Investigation of the Thermoelectric Properties of Boron Carbide-Hafnium Diboride Composite Materials

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Materials

Abstract and Introduction:

In primary energy conversion, it is estimated that only about one-third of the total energy used becomes useful work. Of the two-thirds wasted, the majority is in the form of heat. Thermoelectric modules can be used to directly convert some of this waste heat back to effective use, thus, improving the overall conversion efficiency. Thermoelectric materials research has experienced a renewed interest in recent years as several new candidate materials are being discovered and optimized. One class of materials that have emerged for use in high temperature thermoelectric applications is borides. Borides such as boron carbide exhibit several favorable mechanical and thermoelectric properties such as high thermal and chemical stability, and a Seebeck coefficient that increases with temperature. The thermoelectric performance of borides can be improved by using composites – usually metal borides [1]. In this work, the effect of hafnium diboride composition on the thermoelectric properties of boron carbide was studied.

Boron carbide-hafnium diboride (B_4C/ HfB_2) composites were prepared by spark plasma sintering (SPS) of a mixture of hafnium diboride powder and boron carbide powder. The boron carbide powder was prepared with a 13.3 wt% composition of carbon, which a previous study found to be the ideal carbon content for the dimensionless figure of merit [2]. The hafnium diboride content was varied between 0 and 20 percent by weight and the effect on the thermoelectric properties was studied. The samples were characterized using x-ray diffraction (XRD). The electrical resistivity and Seebeck coefficient were measured using the four-probe method and differential method, respectively. The thermal conductivity was measured by the laser flash method. The optimal hafnium diboride content was found to be 10 wt%, leading to an improvement in the figure of merit ZT from 0.188 for the non-composite material to 0.200 for the 10% wt HfB_2 composite at 730°C.

Experimental:

Firstly, B_4C powder was prepared with a 13.3 wt% composition of carbon by heating of a boron and carbon powder mixture in an induction tube furnace. This B_4C powder was then mixed with HfB_2 powder to create 0, 5, 10, 15 and 20% HfB_2 by weight samples. The powder was weighed out into 0.7 g samples for sintering and placed into a graphite dye. A SPS system was then used to sinter the composite powders at 1750°C. The sintered pellets were then polished and cut for thermoelectric measurements.

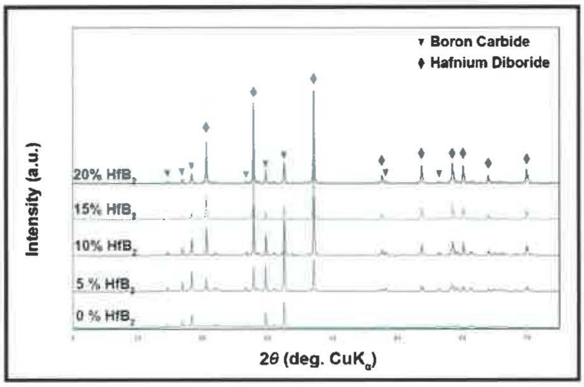


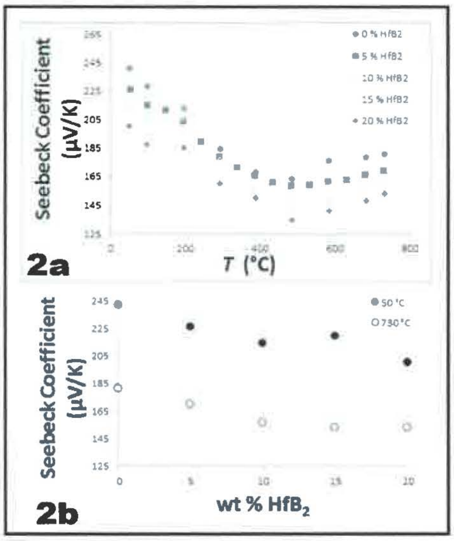
Figure 1: X-ray diffraction data for composite samples showing relative peak heights.

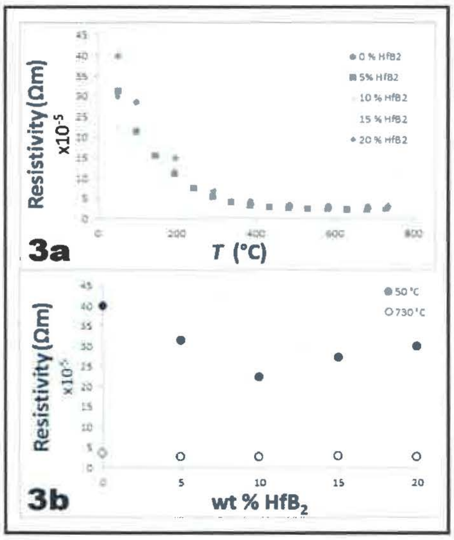
The electrical resistivity was determined by the four-probe method, while the Seebeck coefficient was measured by the differential method. We then used the laser flash method to determine the thermal conductivity of the samples. The samples were ground into a powder for XRD measurements in order to characterize their compositions.

Results and Discussion:

The XRD measurements (Figure 1) were used confirm the composition of the samples based on the peak positions, and height. In addition, the lack of a shift of peak position for each sample indicates that the crystal structure is not affected by the addition of HfB_2.

For all compositions, the Seebeck coefficient first decreases with temperature, then increases with temperature beyond approximately 480°C (Figure 2). The increasing Seebeck coefficient with temperature beyond this point makes boron carbide a favorable material for high temperature applications. It can be seen from Figure 1 that the Seebeck





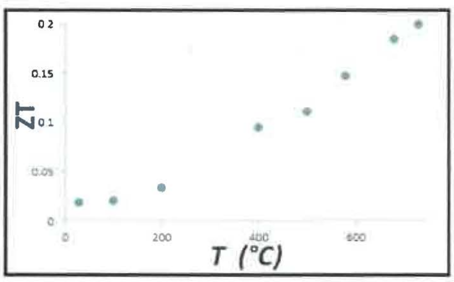


Figure 2, top: Seebeck coefficient as a function of a) temperature, and b) HfB_2 composition.

Figure 3, middle: Electrical resistivity as a function of a) temperature, and b) HfB_2 composition.

Figure 4, bottom: Thermoelectric figure of merit ZT as a function of temperature for 10% HfB_2 sample.

coefficient decreases with increasing HfB_2 composition. This is expected because boron carbide is being replaced by a material with a lower Seebeck coefficient, therefore the overall composite material should have a lower Seebeck coefficient.

Similarly, the electrical resistivity of the samples was compared with changing temperature and composition (Figure 3). The electrical resistivity was found to decrease with temperature for all the compositions examined. The electrical resistivity decreases with increasing HfB_2 content up to 10 wt%, then increases. This result is unusual because the resistivity would be expected to continuously decrease with increasing HfB_2 composition. However, we believe the density of the samples, which was lower than would be expected, is to blame. Further work will be done in order to explain this anomaly.

The thermal conductivity was found to decrease with increasing HfB_2 composition. At 100°C, the thermal conductivity was found to be 4.56 W/mK, 4.52 W/mK and 4.28 W/mK for the 0%, 5% and 10% samples, respectively.

The thermoelectric figure of merit ZT (Figure 4) was found to be the highest for the 10 wt% HfB_2 sample. The ZT value for each sample was found to still be increasing with temperature within the range investigated. The ZT value was increased from 0.188 for the non-composite material to 0.200 for the 10% wt HfB_2 composite at 730°C, an increase of 6%.

Conclusions and Future Work:

The addition of hafnium diboride to boron carbide to form a composite material is a viable means of improving the thermoelectric performance of boron carbide. The measurements show that with an optimum composition, the decrease in the value of the Seebeck coefficient caused by the addition of HfB_2 is countered by the relatively larger decrease in both thermal conductivity and electrical resistivity. The results also show that boron carbide has excellent potential as a high temperature thermoelectric material as the Seebeck coefficient increases with temperature while the thermal conductivity and electrical resistivity decrease with temperature, which leads to a ZT value that increases with temperature.

In the future we hope to fine-tune the optimum composition of hafnium diboride by creating samples that vary by smaller increments of HfB_2 composition. We would also like to measure the thermoelectric properties at higher temperatures as the ZT value is still increasing within the temperature range investigated.

Acknowledgements:

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References:

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[2] Bouchacourt, M., and F. Thevenot. J of Materials Science: 1237-247.