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# Effect of titanium carbide addition on the thermoelectric properties of $B_4C$ ceramics

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## Abstract

$TiB_2/B_4C$  composite ceramics are prepared via hot pressing, in which the  $TiB_2$  particles are formed by introducing  $TiC_{0.78}$  and through the reaction between  $B_4C$  and  $TiC_{0.78}$ . The electrical and thermal conductivities and Seebeck coefficient of samples containing 0, 12.5 and 25.4 vol%  $TiB_2$  are measured from room temperature up to 1200 K. The results show that the transport properties of the samples vary with the  $TiB_2$  content. The transport properties of a 12.5 vol%  $TiB_2/B_4C$  sample are dominated by the  $B_4C$  matrix as in undoped  $B_4C$  ceramics, whilst the transport properties of a 25.4 vol%  $TiB_2/B_4C$  sample are dominated by  $TiB_2$  particles. The figure of merit of the 25.4 vol%  $TiB_2/B_4C$  sample is higher than that of the undoped  $B_4C$  ceramic sample between room temperature and about 700 K, which indicates that it is possible to improve the thermoelectric properties by selecting an optimum combination of different materials. © 2000 Elsevier Science Ltd. All rights reserved.

**Keywords:** A. Semiconductors; D. Electronic transport

## 1. Introduction

Recently, there has been renewed interest in thermoelectric materials [1,2]. The efficiency of a thermoelectric material depends on its material properties through the dimensionless figure of merit  $ZT$  ( $ZT = \sigma\alpha^2T/\kappa$ , where  $\sigma$ ,  $\alpha$ ,  $\kappa$ , and  $T$  are the electrical conductivity, Seebeck coefficient, thermal conductivity and temperature, respectively). For both applications in refrigeration and power generation, the efficiency increases monotonically with  $ZT$  [3]. So far the highest  $ZT$  value of the thermoelectric materials has been about 1, which leads to rather low efficiencies. Hence, until now thermoelectric materials have been only used in applications where reliability or convenience is more important than economy. In order to increase the value of  $ZT$ , many approaches, such as novel alloys [4] and low-dimensional structures [5], have been developed.

Much progress has been made [1,2]. But none of these approaches have yet made a breakthrough.

In the present work, an approach using composite thermoelectric materials, namely  $B_4C$ -based composites, is investigated experimentally. According to an effective-medium theory (EMT) [6], the  $ZT$  of a matrix-based particulate composite is always less than that the biggest  $ZT$  of each component of the composite, which implies that there can be no improvement in  $ZT$  for such particulate composites. However, the EMT prediction may be invalid for the nonmatrix-based composites, such as those with percolation cluster structures. In these systems, if one phase has much higher electrical conductivity than the matrix, the electrical conductivity of the composite can change by several orders of magnitude for a very small change in the volume fraction of the high conducting phase near its percolation threshold ( $\phi_c$ ) [7,8]. Therefore, if the Seebeck coefficient and thermal conductivity for the composite do not change rapidly near  $\phi_c$ , it is possible to get a higher value of  $ZT$  for the composite than that for the matrix.

Boron-rich carbides (e.g.  $B_{6.5}C$ ) are considered as

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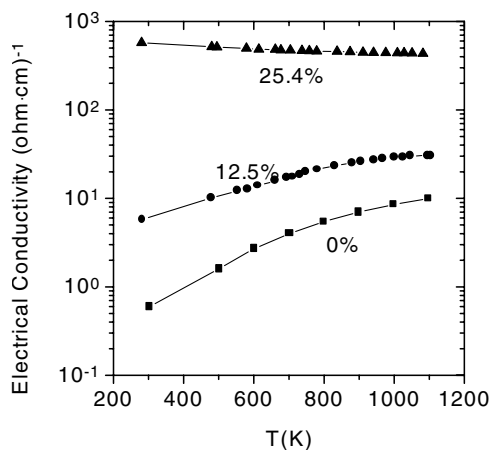
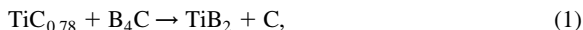


Fig. 1. Electrical conductivity of the samples as a function of temperature.

potential materials for very high temperature thermoelectric energy conversion [9]. Compared with boron-rich carbides,  $B_4C$  has a lower electrical conductivity, a little higher thermal conductivity and almost the same Seebeck coefficient, and thus its ZT is lower than that of the boron-rich carbides. If the electrical conductivity of  $B_4C$  could be increased significantly, while its Seebeck coefficient and thermal conductivity do not change very much,  $B_4C$  would exhibit a larger ZT value [10]. In this paper, we select  $B_4C$  as the thermoelectric (semiconductor) phase and more highly conducting (metallic)  $TiB_2$  as the second phase.  $TiB_2$  is introduced into the  $B_4C$  by adding  $TiC_{0.78}$  and then through the reaction between  $TiC_{0.78}$  and  $B_4C$  [11]:



which occurs at the high temperature, at which the composite was sintered.

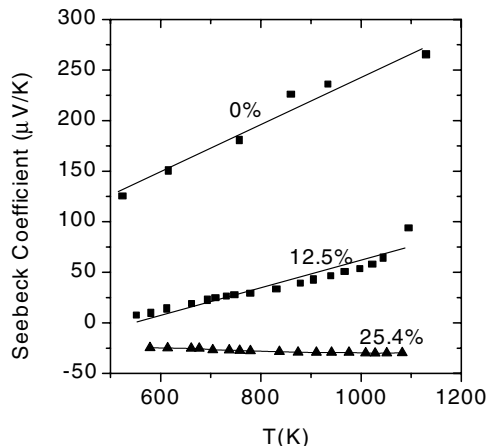


Fig. 2. Seebeck coefficient of the samples as a function of temperature.

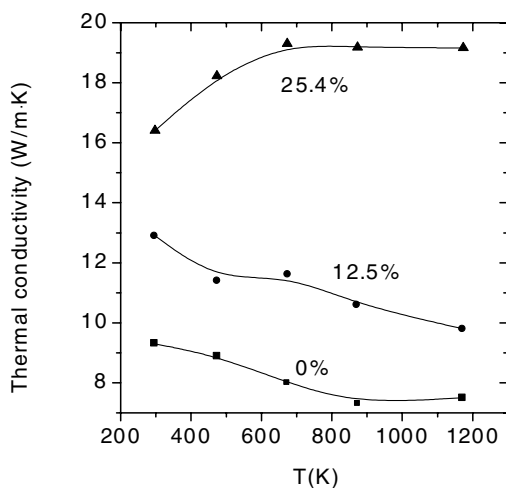


Fig. 3. Thermal conductivity of the samples as a function of temperature.

## 2. Experimental

$B_4C$  powder (average particle size 0.5  $\mu m$ , Moudanjiang boron carbide powder plant, China) was homogenized with various amounts of nonstoichiometric  $TiC_{0.78}$  (average particle size 5  $\mu m$ , Zhuzhou cemented carbide plant, China) by milling the powders together for 10 h. Cylindrical samples were prepared by hot pressing at 1900°C and 35 MPa for 30 min under argon. The pure boron carbide sample was hot pressed at the same temperature for the same time, but at a higher pressure (39 MPa) to get a lower porosity. The electrical and thermal conductivities and Seebeck coefficient were measured up to 1200 K in vacuum. A two-probe method, using a chopped direct current, was employed to measure the electrical conductivity. Seebeck coefficients were determined from the linear relationship between the thermal electromotive force and temperature difference between the two ends of the sample. Thermal conductivity was measured by using the common laser flash method. The apparent porosity of the samples was determined by the method given by the American Society of Testing and Materials Criterion (ASTM C375) [12].

## 3. Results and discussion

From the XRD results, it can be seen that the  $TiC_{0.78}$  is completely converted into  $TiB_2$ . It also shows that the  $TiB_2$  content increases with the amount of  $TiC_{0.78}$  added and that there is very little carbon content compared to the amounts of  $B_4C$  and  $TiB_2$ . The apparent porosity of the samples containing 0, 12.5, and 25.4 vol%  $TiB_2$  is 13.0, 14.0 and 0.82%, respectively. This indicates that adding  $TiC_{0.78}$  can be an effective method of improving the densification of  $B_4C$  ceramics. From scanning electron microscopy

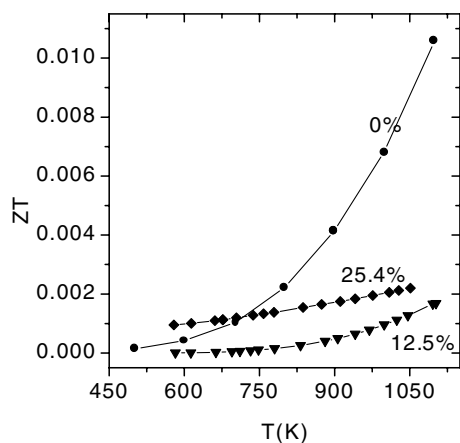


Fig. 4. Dimensionless  $ZT$  of the samples as a function of temperature.

observations, it can be seen that the average grain size of the  $TiB_2$  and  $B_4C$  is nearly the same (about  $1 \mu m$ ).

Fig. 1 shows that the electrical conductivity of the samples increases rapidly with the content of  $TiB_2$ . Note that the electrical conductivity for the 12.5 vol%  $TiB_2/B_4C$  sample increases with temperature as does the undoped semiconducting  $B_4C$  sample. However, the electrical conductivity for the 25.4 vol%  $TiB_2/B_4C$  decreases with temperature, indicating metallic behavior.

The 12.5 vol%  $TiB_2/B_4C$  sample is a p-type semiconductor like the undoped  $B_4C$ , since both Seebeck coefficients remain positive and increase with temperature as shown in Fig. 2. The Seebeck coefficient of the 12.5 vol%  $TiB_2/B_4C$  is always lower than that of the undoped sample at the same temperature. However, the 25.4 vol%  $TiB_2/B_4C$  sample behaves like an n-type material with a negative Seebeck coefficient, whose absolute value increases slowly with temperature.

The thermal conductivity of the samples as a function of temperature is shown in Fig. 3. The thermal conductivity increases monotonically with the amount of  $TiB_2$ , because of the high thermal conductivity of  $TiB_2$  compared with  $B_4C$ . The thermal conductivity for the undoped  $B_4C$  and 12.5 vol%  $TiB_2/B_4C$  samples both decreases with temperature, whereas the thermal conductivity of the 25.4 vol%  $TiB_2/B_4C$  sample increases with the temperature and is nearly constant above about 900 K.

Figs. 1–3 clearly show that the thermoelectric properties change rapidly as the amount of  $TiB_2$  goes from 12.5 to 25.4 vol%, which suggests that conducting phase ( $TiB_2$ ) in the samples becomes continuous in this range and that  $\phi_c$  for  $TiB_2$  is in the range of 0.125–0.254. The transport properties of the 12.5 vol%  $TiB_2/B_4C$  sample are similar to the  $B_4C$ , with the dominant charge carrier being a small polaron ( $B_{11}C^+$ ) [9], because the  $TiB_2$  particles and clusters are isolated in a  $B_4C$  matrix. For the 25.4 vol%  $TiB_2/B_4C$  sample, the conducting phase ( $TiB_2$ ) has a continuous or

percolation path [7,8] through the whole sample and thus dominates the thermoelectric properties of the composite. Therefore, although the electrical conductivity of  $B_4C$  increases with temperature [9], the electrical conductivity of  $TiB_2$  decreases with temperature [13] and the electrical conductivity for the 25.4 vol%  $TiB_2/B_4C$  sample decreases with temperature.

The Seebeck coefficient measurement also shows such changes with  $TiB_2$  content (Fig. 2). The Seebeck coefficient changes from positive to negative value as the content of  $TiB_2$  increases from 12.5 to 25.4 vol%. That is, when the distribution of  $TiB_2$  particles in the composite changes from a dispersed to a continuous state, the dominant conducting mechanism in the composites changes from small polaron hopping to electronic transport. There is also the intriguing possibility that, with a p-type conductor as the second phase, one could obtain p-type  $B_4C$ -based composites. Also because  $B_4C$  (or  $B_xC$ ) is a well-known p-type thermoelectric material, the search for n-type  $B_4C$  (or  $B_xC$ )-based materials has attracted much attention [14,15], but until now it has been unsuccessful. The present work indicates that n-type  $B_4C$  (or  $B_xC$ )-based materials may be obtained by combining a metallic-conducting phase (electronic conductor) with  $B_4C$  (or  $B_xC$ ) in a composite.

The dimensionless  $ZT$ s calculated from the measurements of the electrical conductivity, thermal conductivity and Seebeck coefficient for all the samples are given as a function of temperature in Fig. 4, which shows that the values of  $ZT$  for the 12.5 vol%  $TiB_2/B_4C$  sample are lower than that of the undoped  $B_4C$  sample at all temperatures, as predicted by EMT [6]. However, for the 25.4 vol%  $TiB_2/B_4C$  sample, the values of  $ZT$  are higher than that of the undoped sample below about 700 K, contradicting the EMT prediction [6] and showing that this prediction does not hold necessarily for the percolation system. Note that all the samples have different porosities and that the electrical conductivity, as well as the thermal conductivity of the samples, decreases with porosity, while the Seebeck coefficient of the sample is not very sensitive to porosity [16]. Therefore, the porosity of the present samples probably has no pronounced effect on their  $ZT$  values.

#### 4. Conclusion

The amount of the second conducting phase ( $TiB_2$ ) affects the thermoelectric properties of  $TiB_2/B_4C$  composite ceramics. For the 12.5 vol%  $TiB_2/B_4C$  sample, the value of  $ZT$  is always lower than that of the undoped  $B_4C$  sample, while for 25.4 vol%  $TiB_2/B_4C$  sample, the value of  $ZT$  is higher than that of the undoped  $B_4C$  sample at temperatures below 700 K. This implies that it is possible to get an improvement in  $ZT$  using a continuum percolating composite with an optimized microstructure. Further experiments should be made on composites with volume fractions of  $TiB_2$  closer to the percolation threshold, as well as on other similar

systems such as  $W_2B_5/B_4C$ , or even systems with other semiconducting and conducting phases.

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### References

- [1] T.M. Tritt, M. Kanatzidis, G. Mahan, H.B. Lyon Jr. (Eds.), *Thermoelectric Materials: New Approaches and Advances*, Material Research Society Proceedings, Vol. 478, 1997.
- [2] T.M. Tritt, G. Mahan (Eds.), *Thermoelectric Materials 1998: the Next Generation for Small-scale Refrigeration and Power Generation*, Material Research Society Proceedings, Vol. 545, 1999.
- [3] R.R. Heikes, R.W. Ure Jr., *Thermoelectricity Science and Engineering*, Interscience, New York, 1961, pp. 1–6, 458–517.
- [4] B.C. Sales, D. Mandrus, R.K. Williams, *Science* 272 (1996) 135.
- [5] L.D. Hicks, M.S. Dresselhaus, *Phys. Rev. B* 47 (1993) 12727.
- [6] D.J. Bergaman, O. Levy, *J. Appl. Phys.* 70 (11) (1991) 6821.
- [7] D.S. McLachlan, M. Blaszkewics, R.E. Newnham, *J. Am. Ceram. Soc.* 73 (1990) 2187.
- [8] C.-W. Nan, *Prog. Mater. Sci.* 37 (1993) 1.
- [9] C. Wood, D. Emin, *Phys. Rev. B* 29 (8) (1984) 4582.
- [10] K.-f. Cai, C.-W. Nan, X.-M. Min, *Mater. Sci. Engng B* 67 (1999) 102.
- [11] G.H. Tang, *Symposium Proceeding of 8th Conference of Composite of China, Aviation*, 1994, p. 363.
- [12] ASTM Specification, C 373, *ASTM Standards part 13, American Society for Testing and Materials, Philadelphia*, 1969.
- [13] C.C. Wang, S.A. Akbar, W. Chen, V.D. Patton, *J. Mater. Sci.* 30 (1995) 1627.
- [14] T. Aselage, *Mater. Res. Soc. Proc.* 24 (1991) 145.
- [15] C. Wood, *Symposium Proceeding of APS, Vol. 140, AIP, New York*, 1986, p. 362.
- [16] K.-f. Cai, J.-P. Liu, C.-W. Nan, X.-M. Min, *J. Mater. Sci. Lett.* 16 (1997) 1876.