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The influence of W_2B_5 addition on microstructure and thermoelectric properties of B_4C ceramic

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Abstract

B_4C and B_4C–W_2B_5 composite ceramics are prepared via hot pressing. The composition and microstructure of the ceramics are characterized by means of X-ray diffraction (XRD), electron probe microanalysis (EPMA) and transmission electron microscope (TEM). Their electrical conductivity and Seebeck coefficient are measured from room temperature up to 1500 K. These results show that the values of electrical conductivity for the B_4C–W_2B_5 composite ceramic are much higher than that for the B_4C ceramic, but that the values of the Seebeck coefficient for the composite ceramic are somewhat lower than that for the B_4C ceramic. Both electrical conductivity and Seebeck coefficient increase with increasing temperature. The figure of merit of the composite ceramic is higher than that of the B_4C ceramic, though the thermal conductivity of the B_4C ceramic is somewhat lower than that of the composite ceramic. The reason for the enhancement in the figure of merit of the composite ceramic is discussed.

Keywords: B. Microstructure; D. Boron carbide; Composite ceramic; Thermoelectric properties; Tungsten boride

1. Introduction

Boron-rich carbides (e.g. $B_{6.5}C$) with large Seebeck coefficient (α), moderate electrical conductivity (σ) and low thermal conductivity (κ) at high temperature appear to be promising for very high temperature thermoelectric energy conversion [1]. Compared with boron-rich carbides, B_4C has lower electrical conductivity, a little higher thermal conductivity and almost the same Seebeck coefficient, and thus, its figure of merit Z ($Z = \alpha^2\sigma/\kappa$) is lower than that of boron-rich carbides. But there is no raw material of boron-rich carbides. In order to prepare boron-rich carbides, elemental boron and carbon with high purity must be used. However, high purity elemental boron is very expensive, which leads to the production of boron-rich carbides being more expensive than that of B_4C. It is unfavorable to extend their use. If the electrical conductivity of B_4C could be increased significantly and meanwhile its Seebeck coefficient and thermal conductivity do not change so much, B_4C would be more competitive than boron-rich carbides.

Generally, by forming a composite via doping a second phase which has much higher electrical conductivity than the matrix, the electrical conductivity of the composite will be higher than that of the matrix. A recent theoretical analysis by Bergman and Levy [2] has shown that the figure of merit (Z^*) for such a common matrix based composite is never larger than the greatest value among its pure components, namely:

$$Z^* = \max Z_i, \quad (i = 1, 2, ...) \tag{1}$$

where Z_i denotes the figure of merit for i phase. In spite of the theoretical bound for Z^* of the matrix-based composite, the thermoelectric composites have still attracted much experimental attention [3–5]. In this work, we investigate a B_4C-based composite ceramic. W_2B_5 has high electrical conductivity ($\sigma_{RT} \sim 5.3 \times 10^4$ S cm^{-1}) and can be used as a dopant for B_4C. In order to introduce W_2B_5 into B_4C, we first mill B_4C powder with WC-based cement balls. Because of the high hardness of B_4C, the composition (WC) of the balls is introduced into the B_4C powder by ball wear during the ball-milling,

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and then W_2B_5 particles are produced in situ via the reaction between WC and B_4C during sintering [6,7] and are dispersed in the B_4C matrix. In order to improve the thermoelectric property of B_4C by introducing W_2B_5 into B_4C, the influence of W_2B_5 on microstructure and thermoelectric property of B_4C-based composite ceramic is studied in the present work.

2. Experimental

B_4C powder (average particle size 0.5 μm, Moudanjiang boron carbide powder plant, China) was milled (B_4C:WC based cement ball = 1:10 wt) for 10 h in alcohol and then dried in vacuum. Cylindrical samples (10 mm in diameter, 15 mm in height) were prepared by hot-pressing at 1900°C and 25 MPa for 30 min under argon, in boron nitride-lined graphite dies. During the hot-pressing, graphite end caps (10 mm in diameter and 1 mm in thickness) were bonded to the cylinders, which facilitates attachment of platinum electrodes (10 mm in diameter, 0.3 mm in thickness) located at the two ends of the sample and prevents the reaction between B and Pt. Thermocouple and electrical leads for Seebeck coefficient and electrical conductivity measurements were soldered on the slices of the platinum electrode. Electrical conductivity and Seebeck coefficient measurements were carried out by using a computer control testing system up to 1500 K under argon. Two-probe method with chopped direct current was employed to measure the electrical conductivity. Seebeck coefficient was determined by the slope of the linear relationship between the thermal electromotive force and temperature difference (about 10–15 K) between the two ends of the specimen, which was caused by cooling one end of the sample using cold argon. The error of the Seebeck coefficient measurement is about 10%. Thermal conductivity was measured by using the common laser flash method on 2–3 mm thick slices. The density and apparent porosity of the samples were determined by the method given by the American Society of Testing and Materials Criterion (ASTMC375 [8]). XRD, EPMA (JXA-8800R type) and TEM (Philips CM 12 TEM/STEM + PV9100/70 type) were used for characterization of the samples.

3. Results and discussion

Fig. 1 is the XRD spectrum of the sample with raw B_4C powder milled. Besides the peaks for B_4C, there are three new peaks which correspond to the characteristic peaks for W_2B_5. The strongest peak for W_2B_5 is just in superposition with the second stronger peak for B_4C. It indicates that WC is introduced into B_4C powder during the ball milling and reacts with B_4C during the sintering to form W_2B_5 [6]. The density and apparent porosity of the sample with W_2B_5 (about 2 wt%) and without W_2B_5 are 1.9910 and 1.5729 g/cm^3 and 21.4 and 37.7%, respectively. It can also be seen from the second electron images for the samples that the sample with W_2B_5 is more densified than the sample without W_2B_5, and that the grain size in the sample with W_2B_5 is smaller than that in the sample without W_2B_5, which also indicates that W_2B_5 can inhibit the B_4C grain growth and densify the sample.

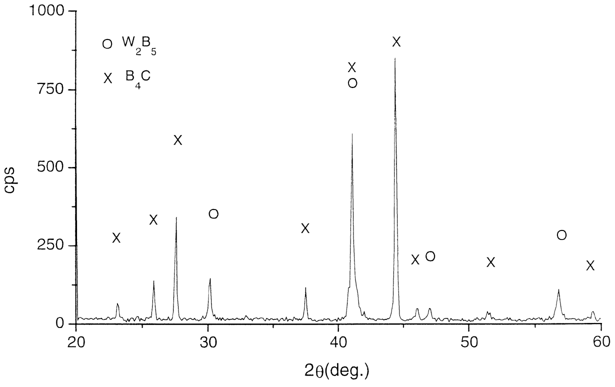


Fig. 1. The XRD spectrum for the sample with W_2B_5.

In order to increase density of the sample without W_2B_5 for comparison with the sample with W_2B_5, B_4C raw powder was hot pressed at 1900°C and 39 MPa for 30 min. The density and apparent porosity of the sample (abbreviated as H) are 2.1935 g/cm^3 and 13.0%, respectively.

The electrical conductivity measured on the samples is shown in Fig. 2 as a function of temperature or reciprocal temperature. It can be seen from Fig. 2(a) that introducing W_2B_5 into B_4C is very efficient to increase the electrical conductivity of the B_4C ceramic. At a given temperature, the electrical conductivity value of the sample with W_2B_5 is several times that of the sample without W_2B_5, and also higher than that of the sample H though the sample H is denser than the sample with W_2B_5. Specially, above 1250 K the electrical conductivity of the sample with W_2B_5 increases rapidly with the temperature. It can be known from Fig. 2(b) that below 1250 K the conductivity-temperature relation of both the samples with W_2B_5 and without W_2B_5 agrees with the prediction by so-called "small polaron hopping" mechanism that the electrical conductivity (σ) is proportional to $T^{-1}\exp(-E_h/kT)$, where E_h is the hopping activation energy [1]. From the values of the activation energy of both samples below 1250 K, it is known that the introduction of a small amount of W_2B_5 into B_4C does not change the electrical transport mechanism.

All samples are P-type semiconductors, since the Seebeck coefficient remains positive and approximately linearly increases with the temperature in the measurement temperature range (Fig. 3). At a given temperature, because W_2B_5 is a metallic-like conductor, the sample with W_2B_5 has a little lower Seebeck coefficient compared with the sample without W_2B_5.

The thermal conductivity of the samples is shown in Fig. 4 as a function of temperature. Fig. 4 shows that the thermal conductivity of the sample without W_2B_5 is almost independent of temperature in the measurement temperature range and the more densified of the sample without W_2B_5, the higher thermal conductivity, and that introducing W_2B_5 into B_4C increases the thermal conductivity because of higher thermal conductivity of W_2B_5 than B_4C.

Fig. 5 presents the values of the figure of merit calculated from the measurements of the electrical and thermal conductivities, and the Seebeck coefficient for these samples. These results show that Z monotonicaly increases with temperature. Furthermore, as the temperature is below 1000 K, the values of the figure of merit for the sample with W_2B_5 and sample H are nearly the same, but higher than that for the sample without W_2B_5; while above 1000 K the Z values for the sample with W_2B_5 are much higher than those for both samples without W_2B_5. It indicates that if the samples with and without W_2B_5 have the same porosity the Z values for the former are higher than that for the later.

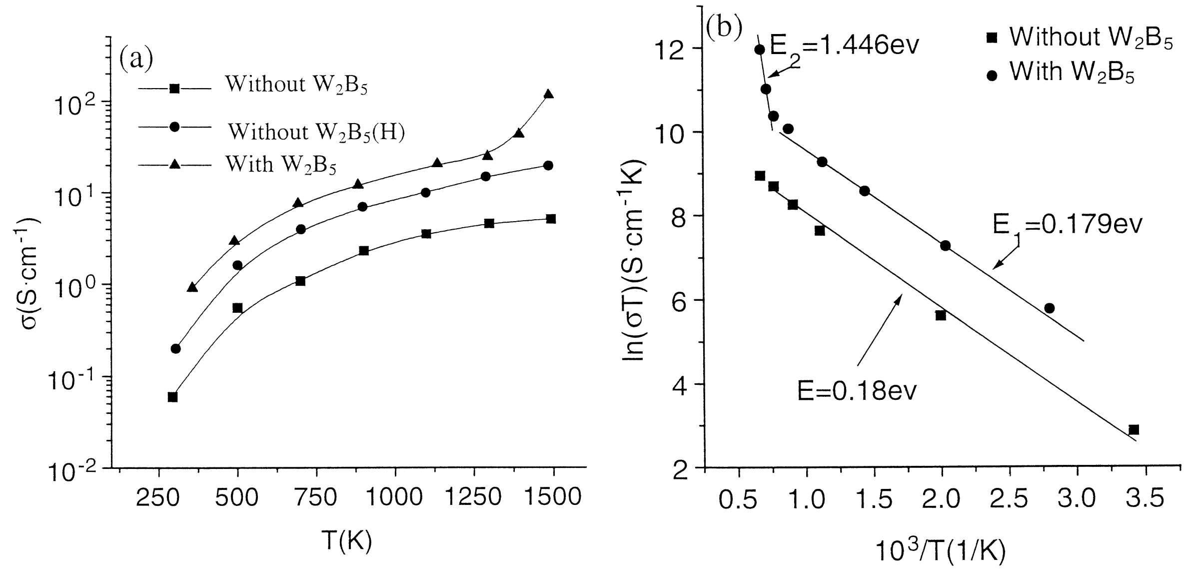


Fig. 2. Temperature dependence of electrical conductivity for the samples.

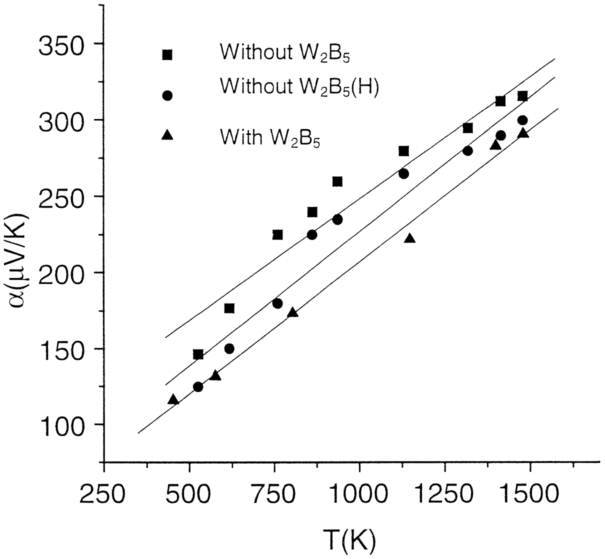


Fig. 3. Temperature dependence of Seebeck coefficient for the samples.

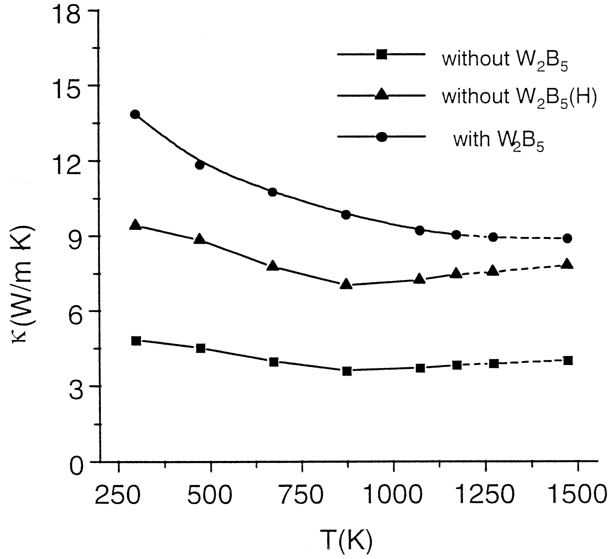


Fig. 4. Temperature dependence of thermal conductivity, where solid lines denote the measurement data and dotted lines are extrapolated data.

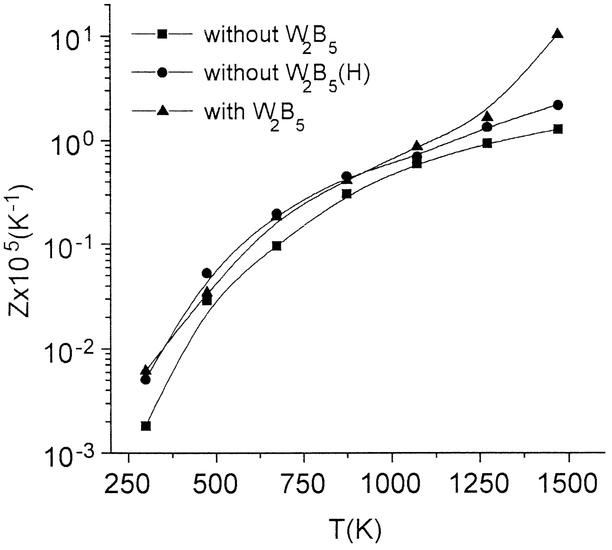


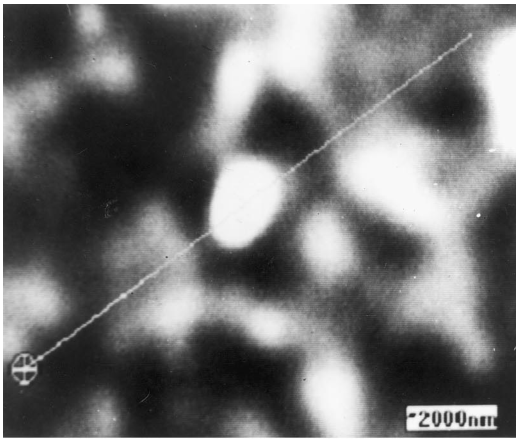
Fig. 5. Temperature dependence of figure of merit for the samples.

The results above indicate that introducing W_2B_5 into B_4C can improve the figure of merit of B_4C ceramic, which is beyond the simple theoretical bound by Bergman-Levy analysis [2]. The sample with W_2B_5 was further analyzed in order to understand the reason. Fig. 6a is its typical microstructure. From the EDAX analysis, it is known that the light grain located in the center of Fig. 6a is a W_2B_5 grain. There is a strong W peak corresponding to the W_2B_5 grain (Fig. 6b). It is of interest to note that there are two little peaks corresponding to the two B_4C grains at the each side of the W_2B_5 grain, which implies that there is a little content of W_2B_5 at the surface of the two B_4C grains.

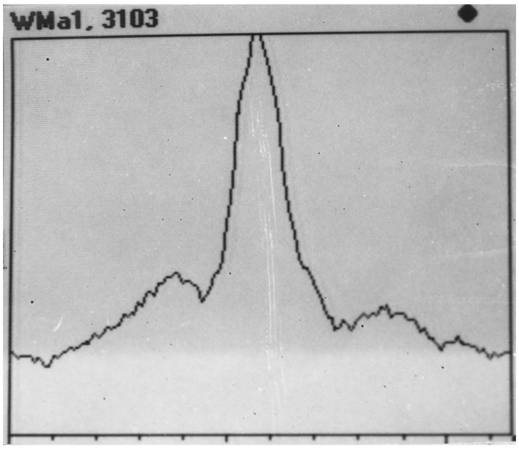
From the TEM observation of the sample, there is a dim second phase grains that locate at the triples of B_4C grains. A few B_4C grains contain impurities that mainly consist of Fe, Co and Cr, probably from WC based cement balls. The EDAX analysis results corresponding to the substance at the triple (1 in Fig. 7a), grain boundary (2 in Fig. 7a) and at the center of B_4C grain (3 in Fig. 7a) are shown in Fig. 7b. It can be concluded from Fig. 7 and the XRD analysis result (Fig. 1) that the substance at the triple is W_2B_5, and it can be known from the Fig. 7b that the grain boundary near the triple contains a little amount of W_2B_5, which further evidence the result of EPMA (Fig. 6).

The reaction between B_4C and WC starts at about 1000°C and ends at 1400°C [6]. From the EPMA and TEM analyses, the formation mechanism of the special grain interface between B_4C and W_2B_5 is suggested as below. At the beginning of sintering, WC grain is situated at the hole formed by B_4C grains. At the temperature is about 1000°C, atom W in the WC grain diffuses toward B_4C grains that are surrounding the WC grain, while atom B in the B_4C grains diffuses toward WC grain. Inter-diffusion of B and W leads to the formation of a film of W_2B_5 on the surface of the WC and B_4C grains. Because in the system the concentration of atom B is higher than that of atom W with larger size and weight, atom B diffuses faster than atom W. Atom B keeps diffusing toward WC and reacts with atom W, which diffuses outward from the center of the WC grain since there is a difference in the chemical potential between the outer and the center of the WC grain, to form W_2B_5 until the WC is fully changed into W_2B_5. Because no atom W further diffuses toward B_4C, there is only a film of W_2B_5 on the surface of the B_4C grains. On the other hand, the formation of W_2B_5 particles may produce defects such as dislocation in B_4C matrix.

A special grain interface between the matrix (B_4C) and the dispersed phase (W_2B_5) and the effect of W_2B_5 particles are probably main reasons for the Z values of our composite ceramic being beyond the theoretical bound by Bergman and Levy's simple analysis which assumed a perfect inclusion-matrix interface and no change in properties of the matrix.

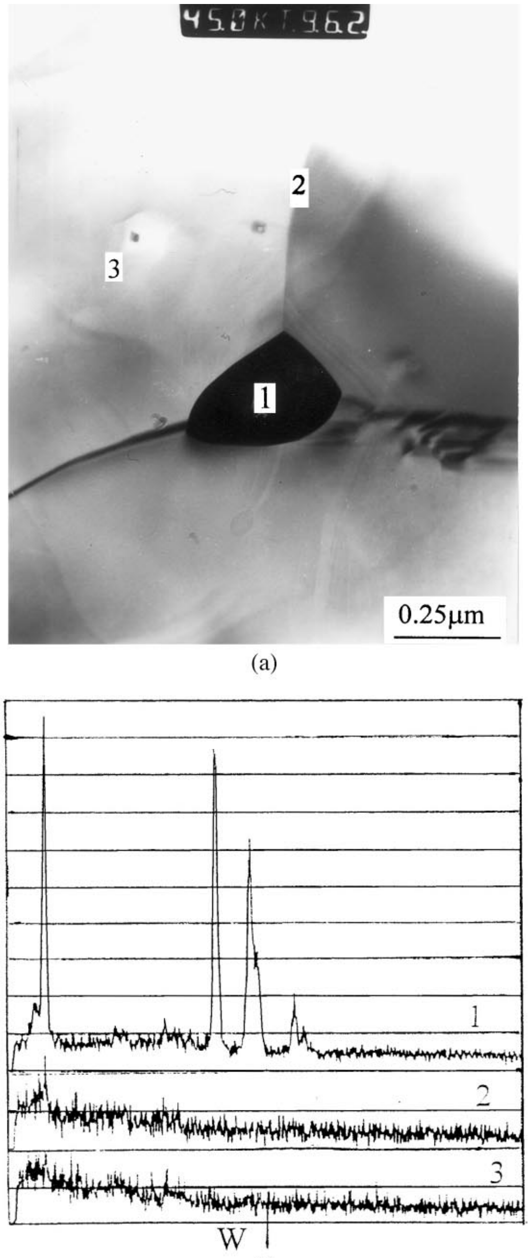


(a)



(b)

Fig. 6. Second electron image of the sample with W_2B_5 (a), line scanning image of W element (b) corresponding to the scanning line (diagonal in Fig. 6a).



(a)

(b)

Fig. 7. (a) TEM of the sample with W_2B_5 and (b) EDAX results responding to those sites indicated in (a).

4. Conclusions

By introducing W_2B_5 into B_4C, the thermoelectric property of the B_4C ceramic has been improved. The figure of merit for the W_2B_5–B_4C composite ceramic is found to be higher than that for B_4C, and is about 1.03×10^{-4} K^{-1} at 1500 K, because the composite ceramic is formed not by simply mixing B_4C and W_2B_5. The present results show that it is possible to improve the thermoelectric property of a material by means of introducing a second dispersed phase into the material, which is due mainly to the effect of dispersed particles on the microstructure of the material.

Acknowledgements

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