

Microstructure and Thermoelectric Properties of B-C-Y System Composites

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B-C-Y system composites were prepared by arc-melting using B, B_4C and YB_6 powders. A phase diagram of the B-C-Y system at a B-rich region was determined. A two-phase region of B_4C - YB_6 is a pseudo-binary eutectic system whose eutectic composition is about 40 mol% YB_6 . In the B_4C - YB_6 composites, the electrical conductivity and the thermal conductivity increased with increasing the YB_6 content. B_4C - YB_6 composite containing about 5 mol% YB_6 have the greatest dimensionless figure-of-merit (ZT) value of 0.54 at $T=1100K$.

Key words: thermoelectric, boron carbide, yttrium boride, eutectic, phase diagram

1. INTRODUCTION

Boron carbide (B_4C) is candidate thermoelectric material at high-temperatures because of its high Seebeck coefficient, low thermal conductivity and moderate electrical conductivity [1]. However, the performance of B_4C should be more improved for practical applications. Since the thermoelectric properties of B_4C strongly depend on the microstructure [2], it could be effective to make composites by dispersing a second phase in the B_4C matrix for increasing the Z value of B_4C [3].

There are several yttrium borides such as YB_{66} , YB_{12} , YB_6 , YB_4 and YB_2 [4, 5]. It is known that YB_{66} is a semiconductor with a significantly low thermal conductivity [6-8], and YB_4 , YB_6 and YB_{12} are metallic conductors. However, the ternary B-C-Y phase diagram is uncertain, and the thermoelectric properties of the B-C-Y system composites have not been published. In the present work, we prepared B-C-Y system composites by arc-melting at a B-rich region, and found that the dispersion of YB_6 in the B_4C matrix significantly improved the thermoelectric performance of the B_4C at high temperatures.

2. EXPERIMENTAL PROCEDURE

B, B_4C and YB_6 powders were weighed and mixed in an agate mortar with a small amount of methanol. The composition on the B_4C - YB_{66} , B_4C - YB_{12} and B_4C - YB_6 tie-lines were prepared as shown in Fig. 1. The mixed powders were pressed to pellets, and arc-melted with a tungsten electrode in an argon atmosphere.

The crystal structure and lattice parameters of the arc-melted specimens were examined by powder X-ray diffraction ($CuK\alpha$). The microstructure was observed by scanning electron microscopy (SEM) and electron probe microanalysis (EPMA). The density was determined by the Archimedeian method in toluene. The electrical conductivity (σ) was measured with a four-probe method in a flowing argon gas. Seebeck coefficients (α) were measured in a vacuum by an ac method [9]. The thermal conductivity (κ) was measured with a laser-flash technique in a vacuum. The Hall mobility and carrier concentration were

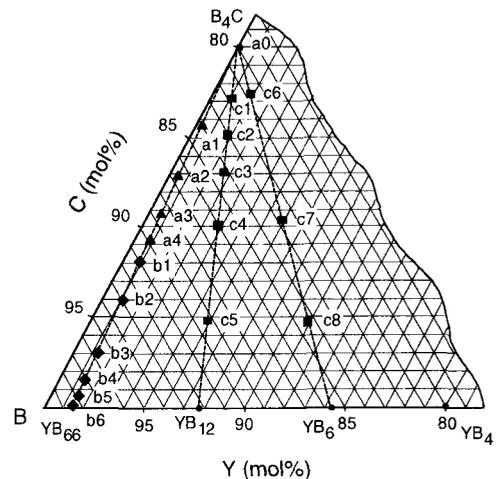


Fig. 1 Compositions of specimens prepared in the present work.

evaluated by the van der Pauw's method in a vacuum. All the measurements were carried out from 300 to 1100K. The figure-of-merit (Z) values were calculated from the formula of $Z=\alpha^2\sigma/\kappa$.

3. RESULTS AND DISCUSSION

3.1. Microstructures

In the a1 to a4 specimens (see Fig. 1), B_4C is the main phase containing YB_6 . The c1 to c4 specimens also consisted of B_4C and YB_6 phases. This shows that these specimens are in a binary B_4C - YB_6 region. The c6 to c8 specimens were mixtures of B_4C , YB_6 and YB_4 , which suggests that these specimens are in a ternary B_4C - YB_6 - YB_4 region. The c5 specimen consisted of three phases of B_4C , YB_{12} and YB_6 . According to the SEM and EPMA analysis, the B_4C - YB_6 system is pseudo-binary eutectic, in which the eutectic composition is about 40 mol% YB_6 . The b1 to b6 specimens are mixtures of YB_{66} and B_4C . In the specimens of a2 to a4 and c2 to c4, small amounts of YB_{12} and/or YB_{66} were observed. However, by annealing these specimens at 1700K, the YB_{12} and YB_{66} phases were disappeared. Therefore, YB_{12} and YB_{66} phases in these specimens must be non-equilibrium

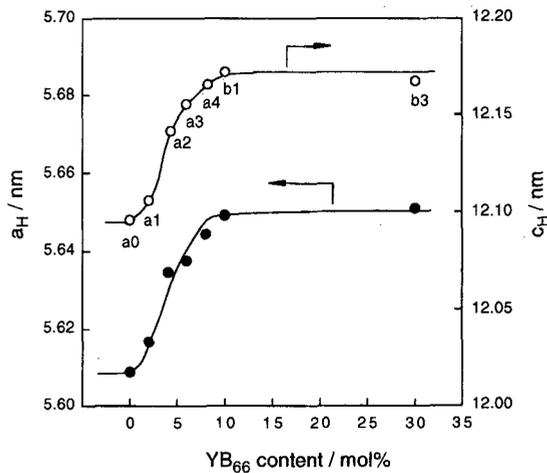


Fig. 2 Effect of YB_{66} content on lattice parameters (a_H and c_H in hexagonal) of B_4C in the specimens on the B_4C - YB_{66} tie-line.

phase. Since there are several peritectic reactions in the B-Y system phase diagram [7], non-equilibrium phases must have been contained in the present work due to sluggish peritectic reactions during the rapid solidification in the arc-melting method.

Fig. 2 shows the change of the lattice parameters (a_H and c_H in hexagonal) of B_4C as a function of YB_{66} content in the specimens on the B_4C - YB_{66} tie-line. Both a_H and c_H values of B_4C increased with increasing the YB_{66} content between the a0 and a4 specimens. They did not change at a higher YB_{66} content more than the b1 specimen. It is well known that B_4C has a wide non-stoichiometric range ($B_{4+\delta}C$; $\delta = 0$ to 5), and the lattice parameters of B_4C increase with increasing the B/C ratio [1]. The a_H and c_H values of B_4C of the specimens of c1 to c4 are almost in agreement with those estimated from the $B_{4+\delta}C$ - YB_6 tie-line. This suggests that there might be no solid solution of Y in

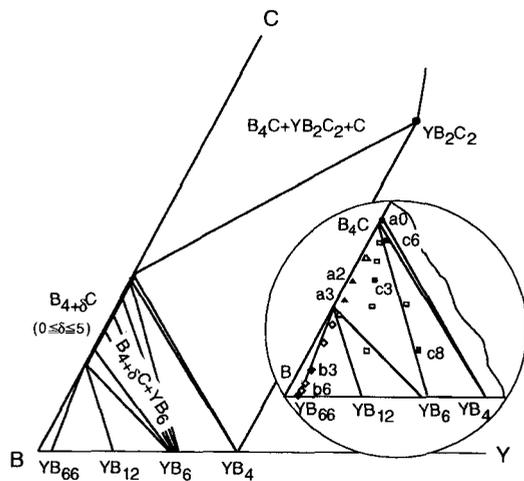


Fig. 3 A proposed phase diagram of B-C-Y system in the boron-rich region. (thermoelectric properties of the specimens in the circle are indicated in this paper)

$B_{4+\delta}C$. It is reported that YB_6 has a slight B-rich non-stoichiometric range forming Y vacancies [10]. The non-stoichiometric range of YB_{66} could be YB_{20} to YB_{100} . However, most researchers express the YB_{20-100} as YB_{66} [4,6]. A phase diagram of B-C-Y system in the boron-rich region assumed from the present work is presented in Fig. 3.

3.2. Thermoelectric properties

We have measured the thermoelectric properties of all specimens indicated in Fig. 1. As typical examples, we report the results on the specimens of a2, a3, b3, b6, c3, c6, c8 and a0 (B_4C) in this paper.

Fig. 4 shows temperature dependence of the electrical conductivity (σ). In the a2 and a3 specimens, which are mainly B_4C , the σ values and their temperature dependence were almost the same as those of B_4C . In the b3 and b6 specimens, where YB_{66} is the main phase, the σ values were significantly lower than those of B_4C . A YB_{66} single crystal has σ values of 10^{-3} to 10 S m^{-1} at room temperature to 1100K [9], which are far lower than that of B_4C . The specimens of c6 and c8 are mixtures of B_4C and YB_6 ; the σ values increased with increasing YB_6 content, showing metallic conduction. The c6 specimen had significantly high σ values in spite of the small amounts of YB_6 (only several mol%). It is uncertain why such a small amounts of YB_6 is effective to increase the σ values.

Fig. 5 shows temperature dependence of Seebeck coefficients (α). The polarity of α of all the specimens is positive indicating the hole conduction. The α values of the a2 and a3 specimens increased with increasing temperature. The highest α value of 500 $\mu V K^{-1}$ at 1100K for the a2 specimen was almost twice as that of B_4C . Fig. 6 represents the temperature dependence of the Hall mobility and the carrier concentration of the a0

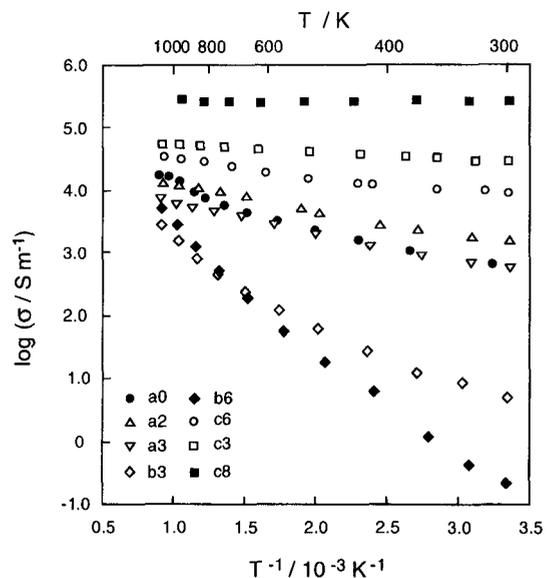


Fig. 4 Temperature dependence of electrical conductivity (σ) for the B-C-Y system composites.

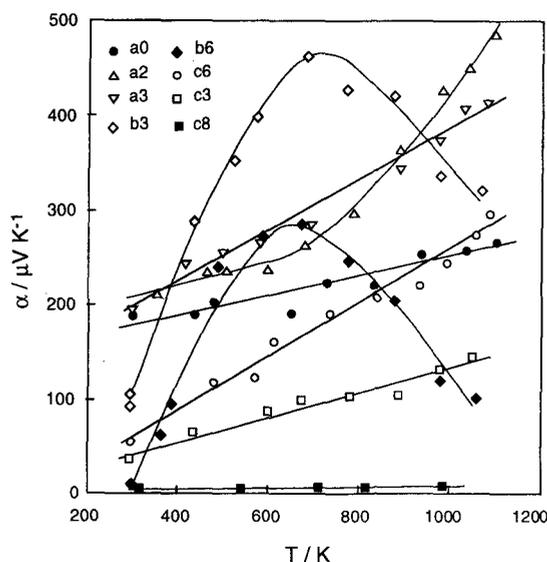


Fig. 5 Temperature dependence of Seebeck coefficients (α) for the B-C-Y system composites.

(B_4C) and the a2 specimens. The carrier concentration of the a2 specimen was slightly smaller than that of B_4C , but the Hall mobility of the a2 specimen was about 10 times greater than that of B_4C . We observed that stacking faults formed at the B_4C /second phase boundary and extended to the B_4C matrix. This may contribute the increase of α values. Further microstructural observation is under way. In the b3 and b6 specimens, which mainly consist of YB_{66} phase with a small amount of B_4C , the α values showed the maximum at about 700K. The same trend was reported in other B-rich borides such as SmB_{66} , DyB_{66} and

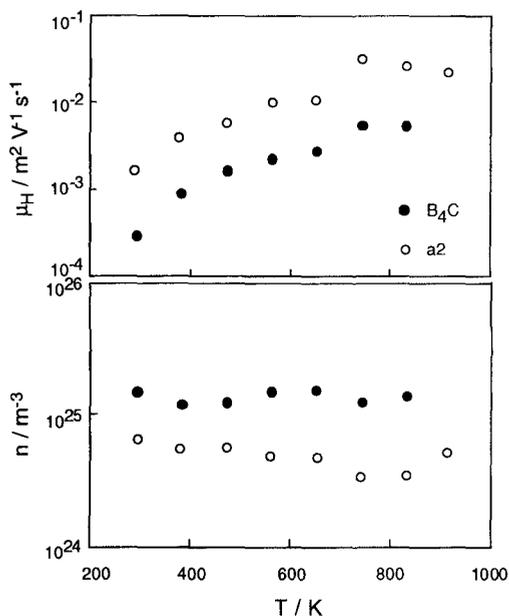


Fig. 6 Temperature dependence of Hall mobility and carrier concentration of B_4C and the a2 specimen.

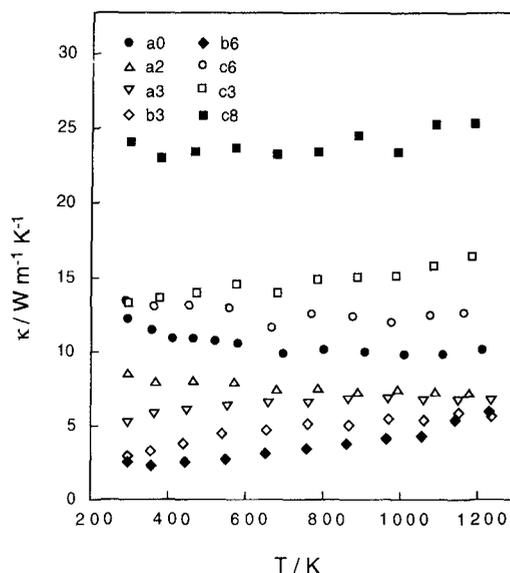


Fig. 7 Temperature dependence of thermal conductivity (κ) for the B-C-Y system composites.

amorphous B [7]. In a YB_{66} single crystal, the temperature showing the maximum of α was 300K, and the greatest α value was about $800 \mu V K^{-1}$. The α values of the c3, c6 and c8 specimens decreased with increasing the YB_6 content.

Fig. 7 shows temperature dependence of thermal conductivity (κ). The κ values of all the specimens were almost independent of temperature. The κ values of the a2 and a3 specimens were smaller than those of B_4C . The B content in the B_4C phase in these specimens is greater than $B/C=4$ as indicated previously. The κ values of B_4C (i.e., $B_{4+\delta}C$) decreased with increasing B/C ratio [11]. Therefore, the decrease of κ values of the a2 and a3 specimens could be caused of high B/C ratios in the B_4C phase. The κ values of the b3 and b6 specimens further decreased. In these specimens, YB_{66} is the main phase, and the κ value of YB_{66} (about $2 W m^{-1} K^{-1}$ at 300K) is much smaller than that of B_4C [8]. The κ values of the c3, c6 and c8 specimens increased with increasing the YB_6 content, and were greater than those of B_4C . The κ value of YB_6 at room temperature was reported as $25 W m^{-1} K^{-1}$ at 300K [12] which is about five times greater than that of B_4C . The increase of κ could be caused of the dispersed YB_6 phase in the B_4C matrix.

Fig. 8 shows temperature dependence of dimensionless figure-of-merit (ZT). The ZT values for most of the specimens except the b3 and b6 specimens increased exponentially with increasing temperature. The b3 and b6 specimens show the maximum at about 700K. The a2 specimen had the greatest ZT value of 0.54 at $T=1100K$. Fig. 9 shows the comparison of ZT values between several boron-rich borides reported in the literature [1] and that of the a2 specimen. The ZT values obtained in the present work is almost the highest among the boron-rich borides. It was reported that a boron-rich boron carbide ($B_{5.8}C$) had a significantly

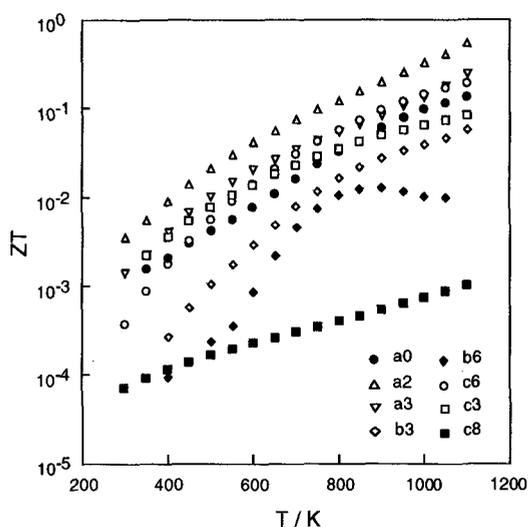


Fig. 8 Temperature dependence of dimensionless figure-of-merit (ZT) for the B-C-Y system composites.

high ZT values [1]. However, the highest ZT value of arc-melted boron carbides in the boron content range between B_9C and B_4C prepared by the present authors was 0.15 at 1100K [11]. Therefore, the dispersed YB_6 phase should associate with the increase of the ZT values in the present work. The microstructure change of B_4C matrix by the dispersed YB_6 phase such as the formation of twin-boundary might have caused the increase of ZT values [2]. Detailed microstructure observation by TEM is under way. The ZT value of the a2 specimen is still increasing exponentially at more than 1100K, and is expected to be more than one at 1200K. This trend is highly promising as the high-temperature thermoelectric material.

4. SUMMARY

B-C-Y system composites, particularly at a B-rich region, were prepared by arc-melting using B, B_4C and YB_6 powders. The microstructure and thermoelectric properties of the composites were studied.

(1) A phase diagram of B-C-Y system in the B-rich region was proposed. A B_4C - YB_6 two-phase region could be a pseudo-binary eutectic system whose eutectic composition is about 40 mol% YB_6 .

(2) In the B_4C - YB_6 system composites, with increasing YB_6 content, the σ and κ values increased but α values decreased. A B_4C - YB_6 composite, in which B_4C is the main phase, showed the greatest ZT value of 0.54 at 1100K. The specimens in which YB_6 is the main phase showed the maximum of ZT values at about 700K.

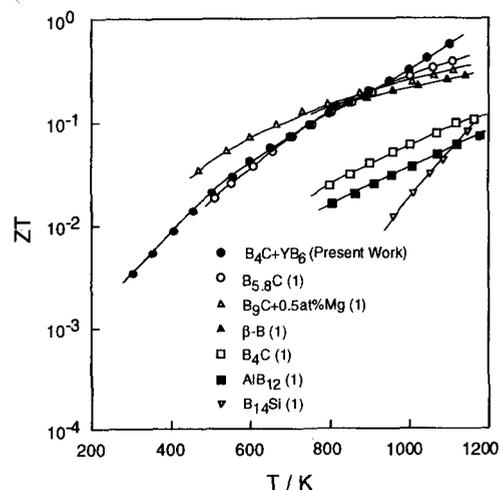


Fig. 9 Temperature dependence of dimensionless figure-of-merit (ZT) for boron-rich borides in a literature and for the a2 specimen.

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