Temperature Dependence of Thermal Conductivity of Boron Carbide at Intermediate and High Temperature

Zhaocen Liu, Zhixue Qu*, Yuan Sun
College of Materials Science and Engineering, Beijing University of Technology, Beijing 100124, China

Corresponding author: quzhixue@bjut.edu.cn

Abstract. The temperature dependence of thermal conductivity of boron carbide (B₄C) at intermediate and high temperature was investigated in this paper. The variation of the inverse phonon mean free path with temperature as well as the density and grain size was investigated to reveal the thermal conduction mechanism of boron carbide. The results show that B₄C undergoes a transition of thermal conduction mechanisms at certain temperature within the range from 473 K to 673K. The transition temperature is just half of the calculated Debye temperature of B₄C. Furthermore, the transition of thermal conduction mechanisms is independent from the density and grain size.

1. Introduction
Boron carbide has attracted much attention in modern engineering due to its low density (the theoretical density is 2.52 g/cm³), high hardness and good chemical stability[1]. Interestingly, boron carbide has also been applied in fast reactor as control rods because of its high neutron absorption cross section, high thermal conductivity and low neutron induced radioactivity[2].

In fast reactor applications, thermal conductivity is one of the most important properties for boron carbide to transfer the heat generated by the (n, α) reaction during the absorption of the neutrons. High thermal conductivity can transfer the heat rapidly and reduce the temperature gradient in the boron carbide pellets which will decrease the thermal stress caused by temperature gradient and extend the service life of control rods. So the value and variation of thermal conductivity of boron carbide pellets is crucial to the service life of control rods.

For the applications in nuclear power industry, the thermal conductivity of boron carbide has been determined by many researchers and the variation of thermal conductivity with temperature has also been investigated. Beauvy et al. have measured the thermal conductivity of boron carbide pellets at different temperatures from 20°C to 1800°C, and proposed a thermal conductivity model involving the dependence on the total porosity and grain size [3]. The temperature dependence of thermal conductivity has also been investigated and a linear relation between the reverse thermal conductivity and temperature was proposed, as shown in equation (1) [1, 3].

\[
\frac{1}{k} = AT + B
\]  

where \( k \) is thermal conductivity, \( T \) is temperature, and \( A \) and \( B \) are the parameters that are independent of temperature.
However, the temperature dependence shown in equation (1) is empirical and was just obtained by mathematical fitting with the experimental data. The variation of thermal conduction behavior and the physical model of thermal conduction are still unknown. Few investigations has been conducted on the thermal conduction mechanism of boron carbide.

As we know, the phonon mean free path plays a significant role in thermal conduction and has a direct relationship with temperature. So it has been considered as a good tool to investigate the thermal conduction mechanism [4]. On the other hand, the total porosity and grain size are also important factors to influence the variation of thermal conductivity of boron carbide. In this paper, two series of boron carbide samples with different density and grain size were prepared and the thermal conductivities were measured. The phonon mean free path for different samples were calculated from the thermal diffusivity data, and the variation of phonon mean free path with temperature as well as the density and grain size was investigated to reveal the thermal conduction mechanism of boron carbide.

2. Experimental

2.1. Materials

All the samples of boron carbide were prepared by hot-pressing sintering process. Powders with an average particle size of 4.031 μm (Dalian Boronten Technology Co., Ltd) were used as starting materials. In the sintering process, the heating rate was 20°C/min under 1000°C, and then reduced to 10°C/min within the temperature range from 1000°C to 1600°C, followed by a lower heating rate of 5°C/min from 1600°C to the holding temperature.

The limited mold method was used to control the densities of boron carbide samples. Samples with densities of 2.1, 2.2, 2.3 and 2.4 g/cm³ were prepared at 1900, 1950, 2000 and 2050°C, respectively. To investigate the effect of grain size, two series of samples were hot-pressed under a pressure of 30 MPa for 15 min (1#) and 60 min (2#), respectively.

2.2. Characterization

The bulk density ($\rho$) of the samples was measured using the Archimedes technique, with the immersion medium being deionized water. The total porosity was calculated according to the theoretical density of boron carbide (2.52 g/cm³). The microstructure characterization of the samples was carried out by scanning electron microscopy (SEM, Hitachi S-4800, Japan). The sintered samples were machined, ground and polished, and then thermally etched at 1800°C in vacuum for 30 minutes. The average grain size was estimated by statistical analysis of SEM images after image processing. Since the dwell time is short (15 min), the grain sizes of the 1# samples almost remain unchanged at about 4 μm. Meanwhile, by extending the dwell time to 60 min, the grain sizes of the 2# samples increase to about 5.5 μm.

Thermal diffusivity ($\lambda$) of the samples was measured using the laser flash method (LFA 427, Netzsch, Germany). The measured sample was firstly coated with colloidal graphite on both sides to minimize radiative heat transfer before measurement. The measurement was carried out in a pure Ar atmosphere from room temperature to 1000°C with an interval of 200°C. The heat capacity ($C_p$) of the samples was obtained from previous literature. The thermal conductivity ($k$) of each sample was then calculated using equation (2) [4]:

$$k = \rho \cdot \lambda \cdot C_p$$

The longitudinal ($v_l$) and transverse ($v_t$) acoustic velocities in the boron carbide sample were calculated by determining the transmission interval between two parallel surfaces of sample using an ultrasonic pulser/receiver instrument (Panametrics,5900PR, US). The average speed of sound ($\overline{v}$) was calculated from the measured longitudinal and transverse acoustic velocities using equation (3) [4]:

$$\overline{v} = \frac{v_l + v_t}{2}$$
3. Results and discussion
The thermal conductivities of all the prepared samples, calculated from measured thermal diffusivities and densities using equation (2), are plotted in Figure 1, which show the temperature dependence of thermal conductivity of 1# and 2# samples with different grain sizes.

![Figure 1. Thermal conductivities of the boron carbide samples with different densities and grain sizes: (a) 1# samples with grain size about 4 μm; (b) 2# samples with grain size about 5.5 μm.](image)

It can be seen from the figure that the thermal conductivity of boron carbide ceramics increases with the increasing density though with a not very good linearity which may be attributed to the systematic error during the measurement process. The variation of thermal conductivity with density is usually caused by the strong scattering of phonons due to the pores in the samples.

Interestingly, the 1# samples with smaller grain size show remarkable larger thermal conductivities than the 2# samples. It means that thermal conductivity of boron carbide increase with the decreasing grain size, which is contrary to the case of most of other ceramic materials. It has also been observed by other researchers [1, 3]. Beauvy et al. speculated that the abnormal variation of thermal conductivity could be the consequence of the precipitation of free carbon in boron carbide pellet as graphite at grain boundaries [3]. The existence of graphite phase on grain boundary may result in a higher thermal conductivity of grain boundary than that of grains. So the decrease of grain size increases the proportion of grain boundary in boron carbide, and thus improves the overall thermal conductivity. However, the existence of graphite phase on grain boundary has not yet been confirmed by experiment. Further work should be done to explain this abnormal variation of thermal conductivity of boron carbide.

It can also be seen from Figure 1 that the thermal conductivity varies from room temperature to 200°C with a lower decrease rate, especially for the 2# samples in Figure 1(b). To further investigate the thermal conduction mechanism, the phonon mean free path $l$ was calculated to show the variation of temperature dependence.

In Debye theory, thermal conductivity of materials can be represented in another form equivalent to equation (2) by the relation [5]:

$$k = \frac{1}{3} C_V \cdot \nu \cdot l$$

(4)
where \( C_p \), \( \overline{\nu} \) and \( l \) represent the heat capacity per unit volume, the average speed of sound and the phonon mean free path, respectively.

As we know, the relation between \( C_p \) and \( C_v \) can be expressed using equation (5):

\[
C_v = C_p \cdot \rho 
\]  

(5)

So, by combining equations (2), (4) and (5), the phonon mean free path can be expressed by equation (6):

\[
l = \frac{3\lambda}{\overline{\nu}}
\]  

(6)

The phonon mean free paths of all the samples were then derived by combining equations (3) and (6) from the data of thermal diffusivity and the average speed of sound. Since the phonon mean free path is usually considered to be inversely proportional to the absolute temperature, the inverse phonon mean free path \( 1/l \) as a function of absolute temperature of all the samples is shown in Figure 2.

![Figure 2](image_url)

**Figure 2.** Inverse phonon mean free path as a function of absolute temperature for the boron carbide samples with different densities and grain sizes. The unit of \( 1/l \) is \( \mu m^{-1} \). (a) 1# samples with grain size about 4 \( \mu m \); (b) 2# samples with grain size about 5.5 \( \mu m \).

It can be seen clearly from Figure 2 that the data of inverse phonon mean free path within the temperature from 473 K to 1273 K show a linear variation with temperature, whereas the value at room temperature deviate from the linear relation, which suggests a transition of the thermal conduction mechanisms near 473 K.

Generally speaking, the phonon mean free path for most of ceramic materials is proportional to \( 1/T \) at a temperature close to or beyond the Debye temperature \( (\Theta_B) \), while it shows a more complicate relation with temperature when the temperature is quite lower than Debye temperature, as shown in equation (7) [5]:

\[
l \propto \exp\left(-\frac{\Theta_B}{\alpha T}\right)
\]  

(7)

Many oxide ceramic materials, such as, \( Al_2O_3 \), \( MgO \) and \( BeO \), have been observed to undergo a transition of thermal conduction mechanisms near the Debye temperature [5]. The inverse phonon mean free paths of these oxides increase faster than the linear relation, which is consistent to the case in Figure 2. The transition temperatures of \( Al_2O_3 \), \( MgO \) and \( BeO \) as well as \( BaC \) in this work have been summarized in Table 1 compared with the corresponding Debye temperatures. The Debye temperature of \( BaC \) was calculated using equation (8) [6]:

\[
l \propto \exp\left(-\frac{\Theta_B}{\alpha T}\right)
\]  

(8)
\[
\Theta_D = \frac{h \nu}{k_B}\left(\frac{3N N_A \rho}{4\pi M}\right)^{1/3}
\]

where \(h\) is Planck's constant, \(\nu\) is average speed of sound, \(k_B\) is Boltzmann's constant, \(N\) is the number of atoms in each unit cell, \(N_A\) is Avogadro's constant, \(\rho\) is density, and \(M\) is molecular weight.

### Table 1. Transition temperatures of thermal conduction mechanisms of several ceramic materials compared with the corresponding Debye temperatures.

| Materials | Transition temperatures/K | Debye temperatures/K |
|-----------|---------------------------|----------------------|
| Al₂O₃     | \(~ 900^a\)               | 1034.9\(^b\)        |
| MgO       | \(~ 710^a\)               | 743\(^c\)           |
| BeO       | \(~ 1400^a\)              | 1280\(^d\)          |
| B₄C       | 473 – 673\(^e\)          | 976.1\(^e\), 949\(^f\) |

\(^a\) Reference [5]; \(^b\) Reference [7]; \(^c\) Reference [8]; \(^d\) Reference [9]; \(^e\) This work; \(^f\) Reference [10].

It can be seen from Table 1 that the transition temperatures of Al₂O₃, MgO and BeO are in the vicinity of the corresponding Debye temperatures. To confirm the transition temperature of B₄C, the data in Figure 2 within the temperature from 473 K to 1273K were linear fitted. Since the data below 473 K are not sufficient to be fitted by equation (7), the data are just connected with a visual line to guide the eye. Compared with the fitted line, the data below 473 K remarkably deviate from the linear relation, which indicates that B₄C goes through a transition of thermal conduction mechanisms at around 473 K. However, this transition temperature is just half of the calculated Debye temperature of B₄C. Taking the error of observation into account, the transition temperature may be higher than 473 K, within the range from 473 K to 673K, which is still much lower than the Debye temperature. However, it is not surprising. Similar case can be observed for SiC that the inverse phonon mean free path increases linearly with temperature from a temperature below 400 K [5], whereas the Debye temperature of SiC is about 1146.3 K [11].

Interestingly, it can be seen clearly from Figure 2 that the data of inverse phonon mean free path in the linear region with respect to temperature will be extrapolated to the same value close to zero for all the samples with different densities and grain sizes. On the other hand, the deviation of inverse phonon mean free path from the linear relation shows a similar trend for all the samples with different densities and grain sizes. It can be considered that the transition of thermal conduction mechanisms is independent from the density and grain size.

### 4. Conclusions

In this work, two series of boron carbide samples with different density and grain size were prepared by hot-pressing sintering and the thermal conductivities of all the samples were measured. The variation of the inverse phonon mean free path with temperature as well as the density and grain size was investigated to reveal the thermal conduction mechanism of boron carbide at intermediate and high temperature. The results show that B₄C undergoes a transition of thermal conduction mechanisms at certain temperature within the range from 473 K to 673K. The transition temperature is just half of the calculated Debye temperature of B₄C. Furthermore, the transition of thermal conduction mechanisms is independent from the density and grain size.

### 5. Acknowledgment

This work was supported by Beijing Natural Science Foundation (2182007) and Youth Talent Project of Beijing Municipal Commission of Education (CIT&TCD201704031).

### References

[1] Wang L S, Fang Y C, Wu F and Yin B Y 2000 Mater. Sci. Eng. Powder Metall. 5 113
[2] Thévenot F 1990 *J. Eur. Ceram. Soc.* 6 205
[3] Beauvy B and Guery M 1983 *Physical properties of boron carbide* CEA-Conf-6652
[4] Qu Z X, Wan C L and Pan W 2012 *Acta Mater.* 60 2939
[5] Kingery WD, Bowen HK, and Uhlmann D R 1976 *Introduction to ceramics*. 2nd ed. New York: Wiley p 617
[6] Anderson O L 1963 *J. Phys. Chem. Solids* 24 909
[7] Chung D H, and Simmons G 1968 *J. App. Phys.* 39 5316
[8] Beg M M 1976 *Acta Crystall.* 32 154
[9] Makurin Y N, Shein I R, Gorbunova M A, Kiiko V S, and Ivanoskii A L 2006 *Refr. Indust. Ceram.* 4 7310
[10] Wang D Y, Yan Q, Wang B, Wang Y X, Yang J M, and Yang G 2014 *J. Chem. Phys.* 140 224704
[11] Jiang M, Zheng J W, Xiao H Y, Liu Z J and Zu X T 2017 *Sci. Rep.* 7 9344