Thermal conductivity of SiC-B₄C materials obtained by reaction-sintering method

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Abstract. In this research, temperature dependences of the thermal conductivity of reaction-bonded SiC – B₄C composite materials at the temperature range of 293 – 1400 K were investigated. The effect of B₄C concentration on thermal conductivity is shown. The thermal conductivity of SiC – B₄C materials were compared with the thermal conductivity of materials based on silicon carbide and boron carbide obtained by different methods.

1. Introduction
Materials based on silicon carbide are widely used in instrumental, metallurgical, ceramic, chemical, and electrical industries because of its unique properties. These materials have high hardness, low density, and outstanding chemical and erosion resistance. High melting points of covalent carbides make them promising for high-temperature applications. Thermal conductivity is one of the most important parameters for materials, which are operating at high temperatures and cyclic heating [1-4].

The thermal conductivity of silicon carbide is highly dependent on the preparation method. The room-temperature thermal conductivity ranges from about 30 - 40 W/(m∙K) for recrystallized and liquid-phase sintered materials to 490 W/(m∙K) for single-crystalline SiC [3].

Due to the high thermal conductivity, materials based on silicon carbide are used in the ferrous and non-ferrous metallurgy as lining blocks and bricks for blast furnaces, muffle, walk-through, rotary and shaft furnaces; as guide rails in blast furnaces and continuous furnaces; in the ceramic industry for receiving capsules, muffles which are used in the sintering of technical ceramics and porcelain; in radio engineering and electronics as a wave absorber, and as protective coatings for nuclear fuel particles, etc.

Boron carbide is widely used in nuclear reactors because of its high neutron absorption cross-section. Because of its high stability at high temperatures and interesting thermo-electrical properties, boron carbide is a promising semiconductor material, for instance, for high-temperature thermoelectric energy conversion. The thermal conductivity of B₄C is lower, then SiC, but it’s quite high if related to most other high-temperature materials [2, 3, 5]. Thereby, the study of the thermal conductivity of composites based on SiC and B₄C is necessary for creating products with optimal combination of mechanical and thermophysical properties [6].

The aim of this research is studying the temperature dependence of thermal conductivity of SiC and B₄C- based materials obtained by the reaction-sintering method.

2. Analytical review
Heat transfer is carrying out by scattering of phonons by different ways, such as:
- scattering by another phonons (phonon-phonon scattering)
- scattering by crystal-lattice defects
- scattering by acceptor atoms

Single-crystalline SiC has high thermal conductivity, gradually decreasing with an increase in temperature (Table 1.)

| Temperature, K | 50  | 100 | 150  | 200 | 300  | 500 | 1000 | 1200 |
|----------------|-----|-----|------|-----|------|-----|------|------|
| Thermal conductivity, W/(m∙K) | 5200 | 2800 | 1500 | 950 | 490  | 240 | 110  | 90   |

In [7] the temperature dependence of thermal conductivity of the single-crystalline silicon carbide 6H-SiC in the temperature interval 25-2000 °C is presented. According to [7] thermal conductivity of monocristalline silicon carbide complies with the regularity $\lambda = 61100/(T-115)$. At the room temperature value of thermal conductivity of the single-crystalline 6H-SiC is $\lambda = 334$ W/(m∙K), at $T=2300$ K this value decreases to $\lambda = 28$ W/(m∙K).

The thermal conductivity of different SiC polytypes studied in [8]. Values of thermal conductivity of cubic 3C-SiC, hexagonal 4H- SiC, and 6H-SiC are respectively $\lambda = 360$ W/(m∙K), $\lambda = 370$ W/(m∙K), and $\lambda = 490$ W/(m∙K).

The grain boundaries, pores and interphase particles in polycrystalline materials are addition sources of phonon scattering. The thermal conductivity of real polycrystalline materials is determined by the concentration of impurities dissolved in the crystal lattice, the concentration of defects in the crystals, the size of the crystals, porosity and other phase components.

The temperature dependences of the thermal conductivity of SiC materials obtained by various methods are shown in Figure 1. The thermal conductivity of a pure single crystal (MSiC) is marked by curve 1. The thermal conductivity decrease from $\lambda = 5200$ W/(m∙K) to about 100 W/(m∙K) during temperature increasing.

Hot-pressed materials with a low content of activating additive [9] has high value of thermal conductivity (HPSiC, curve 2). The values of thermal conductivity of SiC-materials obtained by solid-phase sintering method are lower (Figure 1b, curve 5). The material obtained by activated solid-phase sintering with an addition of 3% wt. of B$_4$C has a high level of mechanical properties and thermal conductivity $\lambda = 120$ W/(m∙K) at room temperature [3].
Effect of oxide additives on thermal conductivity of SiC obtained by liquid phase sintering is determined by values of thermal conductivity of oxides [10-13]. Value of thermal conductivity of the hot-pressed SiC materials decrease to 5–11 W/(m∙K) with the addition of 30 wt. % of the mixture of the Al₂O₃ – Y₂O₃ – CaO system [10]. On the contrary, thermal conductivity increases from 133 to 166 W/(m∙K) with adding a mixture of oxides Y₂O₃ – La₂O₃ from 0.5 to 2 wt. % in the silicon carbide material, and with an increase of the additive above 4 wt. % the value of thermal conductivity begins to decrease [12].

The thermal conductivity of the reaction-sintered materials (Figure 1b, curve 4) depends on the percentage ratio of the polydisperse fractions in the initial silicon carbide powder, the concentration of SiC, C in the finally product, the ratio of primary particles (SiC⁰) and phase of secondary silicon carbide (SiC⁰°) and the density of products [14]. Siliconized (curve 3) graphite has less functional parameters influencing the thermal conductivity, therefore the value of thermal conductivity is higher at room temperature, than at the silicon carbide obtained by the reaction-sintering method (Figure. 1b) [14].

The considered data shows, that materials obtained by the reaction-sintering method, hot-pressing method or chemical gas deposition without pores, with a high content of the main phase have higher values of thermal conductivity. The thermal conductivity of ceramic materials obtained by solid-phase and liquid-phase sintering is significantly lower (Figure 1b).

Figure 2. Temperature dependence of thermal conductivity of boron carbide materials [2, 15].

Thus, the thermal conductivity is influenced not only by the method of obtaining BₓC materials but also by its stoichiometric composition, in contrast to materials based on silicon carbide, which does not have a homogeneity range.

3. Materials and Method

Reaction-sintered materials SiC-BₓC were obtained by the impregnation porous preforms with liquid silicon. Preforms contain particles of primary silicon carbide (SiC⁰), boron carbide (BₓC⁰) and carbon black. The formation of secondary silicon carbide (SiC⁰°) occurs due to the dissolution of carbon and its transport through a silicon melt, and subsequent crystallization on the surface of primary SiC⁰ particles [16].

To obtain the close-packed preforms it is necessary to use powders of different particle size distribution. The experimental compositions presented in table 2. At the stage of mixing the powders into the material were introduced carbon in an amount of 10 wt. % in excess of 100 % of the starting components.
Table 2. Composition of materials studied in this research

| №  | SiC «M5» | B₄C «F180» | Carbon, wt % |
|----|----------|-------------|--------------|
| 1  | 50       | 50          | 10           |
| 2  | 40       | 60          | 10           |
| 3  | 30       | 70          | 10           |
| 4  | -        | 100         | 10           |

The particle size of the powders of silicon carbide and boron carbide was determined by MasterSizer 3000 laser dispersion analyzer: SiC "M5" - d₀.₅ = 3.7 μm; B₄C "F180" - d₀.₅ = 98.8 μm.

Powders in the required ratio (Table 2) with an addition of 10% carbon black in excess of 100% were mixed in a ball mill. The mixture was plasticized, granulated and dried. The obtained powders were pressed in samples 25 mm in diameter × 5 mm high. The infiltration of green bodies by the silicon melt was carried out at 1600°C in a vacuum. The excess of silicon was removed from the surface of samples after sintering by sandblasting.

The density and porosity of the samples were determined by hydrostatic weighing. The elastic modulus was determined by the excitation of resonant vibrations, on the Sound-130 analyzer. The hardness and fracture-toughness coefficient were determined by introducing the Vickers pyramid into the material and measuring the size of the diagonal of the indent and the cracks emanating from it on the PMT-3M microhardness tester. Thermal conductivity was determined on an LFA 457 MicroFlash analyzer, at the temperature range from room temperature to 1400 K. The equipment was provided by the SPSIT Engineering Center.

4. Results and discussion

The porosity of investigated materials depends on the density of the green bodies, the fraction distribution of the initial SiC and B₄C particles, the amount of carbon in the starting mixture, the temperature, and duration of sintering of the samples, in contrast to the reaction-bonded silicon carbide material, usually sintering almost to a non-porous state (P ≤ 0.5 vol.%) [16-19]. The relatively large size of particles of B₄C (d₀.₅ = 90 μm), used for mixtures preparing, limits solving of B₄C particles in a silicon melt.

The increasing of porosity from 1.0 to 1.6% with the increasing of B₄C content (table 3) is caused by the formation of the solid solution B₁₂(C, Si, B). Materials with the highest content of SiC as well as SiC²¹ have highest density: ρ = 2.86 ± 0.02 g/cm³ (99% of theoretical).

The relationship between the density and mechanical properties of materials (Elastic modulus E, fracture toughness coefficient K₁C, Vickers hardness HV) are presented in table 3.

Table 3. Mechanical properties of reaction-bonded materials SiC–B₄C

| №  | ρ±0.02, g/cm³ | H±0.1, % | E±10, GPa | K₁C±0,1, MPa m¹/₂ | HV±0.2, GPa |
|----|--------------|----------|-----------|-------------------|-------------|
| 1  | 2.86         | 1.0      | 384       | 4.4               | 26.8        |
| 2  | 2.80         | 1.1      | 392       | 4.3               | 27.7        |
| 3  | 2.74         | 1.2      | 395       | 4.3               | 28.6        |
| 4  | 2.57         | 1.6      | 411       | 3.8               | 31.5        |

Mechanical properties depend on structural defects (pores, microcracks, etc.). The elastic modulus and Vickers hardness of the reaction-bonded SiC – B₄C materials rise with an increase in the content of B₄C, which have higher values of E or Hᵥµ than SiC. However, an increase in mechanical properties is limited by the formation of brittle phases Si and B₁₂(B,C,Si)₃ at high concentration of B₄C in the
starting mixture. The highest fracture-toughness \( K_{IC} = 4.4 \pm 0.1 \) MPa\( \cdot \)m\(^{1/2} \) was observed at highest content of SiC in the initial mixture.

Experimental temperature dependences of thermal conductivity are decrease at all investigated temperature range (293-1400K) (fig.3). Composition 1 demonstrates decrease in thermal conductivity from 93 W/(m\( \cdot \)K) at room temperature to 22 W/(m\( \cdot \)K) at 1400 K. Relationship \( \lambda = f(T) \) is similar to those of single- and polycrystalline SiC presented in Figure 1 and 2. This result is in good agreement with the data of [20]. In [20] the decreasing temperature dependence of SiC thermal conductivity is explained by the lattice component – phonon-phonon scattering. The most significant effect of a decrease in the thermal conductivity with increasing temperature observed in the range 273–800 K. The decrease in the thermal conductivity slows down with a further increase in temperature.

The concentration of boron carbide in composites predictably affects their thermal conductivity because of higher thermal conductivity of SiC compared to B\(_4\)C (Figure 1 and 3). Thermal conductivity gradually decreases over the entire temperature range with an increase in the content of B\(_4\)C in the initial mixture from 50 to 100 mass. %. At room temperature, the effect of B\(_4\)C concentration on the thermal conductivity of composites is most significant. An increase in the content of boron carbide in the initial mixture from 50 to 100 mass. % contributes to a decrease in thermal conductivity from 93 W/(m\( \cdot \)K) (composition 1) to 46 W/(m\( \cdot \)K) (composition 4). At high temperatures, the effect of B\(_4\)C concentration on thermal conductivity is less significant. At 1400 K, the thermal conductivity of these compositions decreases from 22 (50% B\(_4\)C) to 13 W/(m\( \cdot \)K) (100% B\(_4\)C). The observed decrease of the thermal conductivity of SiC – B\(_4\)C composites with an increase in the concentration of B\(_4\)C is associated not only with the additive effect, but also with the influence of the porosity of materials. With an increase in the content of B\(_4\)C in the initial mixture from 50 to 100 mass. % porosity of reaction-sintered ceramics increases from 1 to 1.6%, which makes a certain contribution to the overall decrease of thermal conductivity. A similar effect of decreasing of thermal conductivity of reaction-sintered SiC ceramics was previously observed in [4] and [21].

5. Conclusion
The thermal conductivity of the reaction-bonded SiC – B\(_4\)C composite materials was studied in the temperature range from room temperature to 1400 K. The dependence is decreasing in the entire temperature range. The effect of a decrease of thermal conductivity with an increase of the concentration of boron carbide in the initial mixture was established. The effect of porosity on the
The value of thermal conductivity is noted. Composites with a maximum silicon carbide content have the highest thermal conductivity of $\lambda_{20} = 93 \text{ W/(m} \cdot \text{K)}$.

**Acknowledgments**
This research was carried out with financial help of Russian Foundation for Basic Research 17-03-00863 A.

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