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Low pressure hot pressing of B_4C matrix ceramic composites improved by Al_2O_3 and TiC additives

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ABSTRACT

B_4C matrix ceramic composites toughened by Al_2O_3 and TiC were prepared by low pressure hot pressing. The relative density, Vickers hardness, fracture toughness and flexural strength of the new fabricated composites were measured. Microstructure observations of the fracture surfaces and the indentation cracks of the B_4C matrix ceramic composites were analyzed, and an X-ray diffraction phase analysis was performed. The experiment results showed that chemical reactions took place during the low pressure hot pressing process and resulted in the $B_4C/Al_2O_3/TiB_2$ composite. The densification rate of the B_4C matrix ceramic composites was enhanced and the mechanical properties were improved via the introduction of Al_2O_3 and TiC additives. The Vickers hardness, fracture toughness and flexural strength of the composite with the addition of 4.7 wt.% Al_2O_3 and 10 wt.% TiC were 24.8 GPa, 4.8 MPa $m^{1/2}$ and 445 MPa, respectively.

1. Introduction

Boron carbide possesses an excellent hardness, outstanding elastic modulus, a low specific gravity, high wear resistance, high melting point, good chemical inertness, and so on, making it a promising engineering ceramic material [1–5]. In particular, boron carbide is the third hardest technical material after diamond and cubic boron nitride at room temperature. The B_4C matrix ceramic composites manufactured using a high densification rate by hot press sintering are suitable for use as sand blasting nozzles, and they can endure longer erosion-times than other nozzle materials before failing under high blasting conditions [5]. However, monolithic B_4C suffers from a low fracture toughness and flexural strength and poor sinterability due to its high sintering temperature and pressure required for complete densification (which therefore limits its application as an engineering ceramic).

Numerous attempts have been made to overcome the above weaknesses of the material. It has been shown that the addition of a second phase to the B_4C matrix can improve its mechanical properties (such as its strength and toughness), as well as decrease its sintering temperature. In earlier studies, B_4C matrix ceramic composites, e.g., B_4C/TiB_2, B_4C/Al, B_4C/CrB_2, B_4C/Cu, B_4C/(W,Ti)C and B_4C/C, have been developed [1–6]. However, there are few reports on the introduction of Al_2O_3 and TiC in the B_4C matrix to improve its mechanical properties and decrease its hot press sintering temperature. In this paper, B_4C matrix ceramic composites toughened by Al_2O_3 and TiC were fabricated by low pressure hot pressing. The objective of this work was to investigate the effect of Al_2O_3 and TiC on the mechanical properties, microstructure, and sinterability of B_4C matrix ceramic composites. As a result, a method to produce B_4C matrix ceramic composites with a high performance capability after low sintering temperature can be found.

2. Experimental procedure

A commercial B_4C high purity powder with a grain size of 3–5 μm was used as the starting material. TiC and Al_2O_3 with grain sizes of 1–2 μm were used as additives. The amounts and types of impurities in B_4C, Al_2O_3 and TiC are shown in Table 1.

The raw materials were blended with each other in the proportions listed in Table 2, and the combined powders were mixed by wet ball milling in an alcohol medium for 100 h with cemented carbide balls. The container, which is made of cemented carbide, was rotated at a speed of 100 rpm. The average grain size of the final milled powders was less than 1.5 μm. After drying the powder, densification of the compacted powder was accomplished by low pressure hot pressing in a N_2 atmosphere in a graphite die to produce ceramic disks with a diameter of 50 mm and thickness of 6 mm. The hot pressing parameters are listed in Table 2.

The sintered ceramic disks were cut into pieces, and standard test pieces (3 mm × 4 mm × 36 mm) were obtained through rough grinding, finish diamond grinding, and polishing. A three-point-

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Table 1
The amounts and types of impurities in B_4C, TiC and Al_2O_3.

Raw materials	Impurities (wt.%) ≤				
	Free C	B_2O_3	Fe_2O_3	Na_2O	SiO_2
B_4C	0.44	0.4	0.05	–	–
TiC	1.5	–	0.1	–	–
Al_2O_3	0.5	–	0.04	0.1	0.1

flexural mode was used to measure the flexural strength on an electronic universal experimental instrument with a span of 20 mm operating at a crosshead speed of 0.5 mm/min. Six samples, taken from a single ceramic disk, were used to measure the flexural strength of each composition in air at room temperature. The flexural strength was calculated by the following formula [7]:

$$\sigma_f = \frac{3PL}{2bh^2} \quad (1)$$

where σ_f is the flexural strength (MPa) and P is the load (N) under which the samples break, b and h are the width and height (mm), and L is the span (mm).

The relative densities of the composites were calculated according to the equation:

$$\rho_R = \frac{\rho_A}{\rho_T} \quad (2)$$

where ρ_R is the relative density, ρ_A is the actual density (cm^3) of the sintered sample, and ρ_T is the theoretical density (cm^3) of the composite. The actual density ρ_A was obtained according to the expression:

$$\rho_A = \frac{M}{V} \quad (3)$$

where V is the volume (cm^3) of the distilled water that the sintered sample drains and m is the mass (g) of the same sample. The value of the theoretical density ρ_T depends on the composition of the composite, and was calculated by the following formula:

$$\rho_T = \sum \rho_i \cdot V_i \quad (4)$$

where ρ_i and V_i are the theoretical density and volume content of each composition, respectively.

The composite's Vickers hardness was measured on a polished surface with a load of 9.8 N for 5 s with a micro-hardness tester. The fracture toughness measurement was performed using an indentation method with a hardness tester, and the results were obtained according to the formula proposed by Cook and Lawn [8]. An XRD analysis was performed to identify the crystal line phases after sintering. The fracture surfaces' and polished surfaces' microstructures were studied by scanning electron microscopy.

3. Results and discussion

3.1. X-ray diffraction phase analysis

The X-ray diffraction analysis of samples T1, T2, T3, T4 and T5, low pressure sintered at 1900 °C for 60 min, are shown in Fig. 1. It can be seen that B_4C and C exist in sample T1, where the C may come mainly from the graphite die. No trace of TiC was found in any of the composite samples, and B_4C, TiB_2, C and Al_2O_3 are visible in the B_4C matrix ceramic composites, where TiB_2 and some of the C were formed by the following reaction:

$$B_4C + 2TiC \rightarrow 2TiB_2 + 3C \quad (5)$$

According to the thermo-chemical data [9] for the B_4C–TiC system, the Gibbs free energy (ΔG_θ^T) of Eq. (5) at 1900 °C was −200.800 kJ/mol. Therefore, the reaction described by Eq. (5) probably took place during the low pressure hot pressing process.

As C was thought to react with B_2O_3, an impurity in B_4C, the following reaction may have occurred [10]:

$$2B_2O_3 + 7C \rightarrow B_4C + 6CO \quad (6)$$

The value of ΔG_θ^T of Eq. (6) at 1900 °C was −516.039 kJ/mol [9]. Thus, the reaction described by Eq. (6) also probably took place for all the samples during the low pressure hot pressing process.

There was still some C left after reacted with B_2O_3 (Eq. (6)), as seen in Fig. 1. Therefore, B_2O_3 reacted with C completely. In other words, no trace of B_2O_3 existed in samples T1, T2, T3, T4 and T5. The elimination of B_2O_3 contributed to the densification of the B_4C matrix ceramic composites.

It has been reported that B_4C can react with Al_2O_3 and free C by the following chemical reaction [11,12]:

$$6B_4C + Al_2O_3 + C \rightarrow 2AlB_{12}C_2 + 3CO \quad (7)$$

$AlB_{12}C_2$ will be in a molten state at 1900 °C, which may contribute to the enhanced densification rate of the B_4C matrix ceramic composites [11,12]. However, ΔG_θ^T of Eq. (7) at 1900 °C could not be calculated due to a lack of thermo-chemical data for $AlB_{12}C_2$ [9]. There is no trace of $AlB_{12}C_2$ in Fig. 1 (except T1), which indicates either that the process described in Eq. (7) probably did not take place or that the content of $AlB_{12}C_2$ was too small to be detected by XRD analysis.

3.2. Densification rate of B_4C matrix ceramic composites

The relative densities of B_4C matrix ceramic composites with different Al_2O_3 and TiC contents are listed in Table 3. As a function of the low pressure sintering time, the relative density of B_4C matrix ceramic composites increased with an increase in the low pressure sintering time. By comparing T1 with T5, we can see that the introduction of Al_2O_3 appears to enhance the relative density of B_4C matrix ceramic materials. This conclusion is similar to that drawn by Nishikawa and Takagi [13,14]. The relative density of the T3 sample sintered at 1900 °C for 60 min reached 98%, while the density was only 92.4% for monolithic B_4C sintered at 2150 °C for 60 min. These results indicate that the low pressure sintering temperature can be decreased while the relative density is improved through the addition of TiC. There exists high covalent bonding in monolithic B_4C, which makes it difficult to densify. The introduction of TiC might improve the sinterability of B_4C matrix ceramic composites because the existence of TiB_2, produced by the reaction between the

Table 2
Compositions and hot pressing parameters of the samples.

Samples	Compositions (wt.%)			Hot pressing parameters		
	B_4C	Al_2O_3	TiC	Temperature (°C)	Time (min)	Pressure (MPa)
T1	100	0	0	2150	30–75	35
T2	90	5	5	1900	30–75	35
T3	85.3	4.7	10	1900	30–75	35
T4	80.5	4.5	15	1900	30–75	35
T5	94.7	5.3	0	2150	30–75	35