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Effect of alumina addition on the densification of boron carbide ceramics prepared by spark plasma sintering technique

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Abstract

B_4C ceramics have been fabricated by spark plasma sintering (SPS) technology using boron carbide powders and alumina additive. The effects of Al_2O_3 on the densification behavior, microstructure and mechanical properties of the composites were investigated. The addition of alumina as well as the application of SPS technology was found to be beneficial for the densification of B_4C. B_4C ceramics with a small amount of Al_2O_3 exhibiting relative density close to 99% and Rockwell hardness of 90.7 HRA could be prepared by SPS method at 1750 °C.

Keywords: B_4C; Densification; Microstructure; Rockwell hardness; SPS

1. Introduction

Boron carbide based materials are increasingly used in several industrial sectors, particularly for neutron absorption, armor, thermoelectric and cutting tools due to the combination of their high melting point, remarkable hardness, low density, wear resistance, chemical stability, neutron absorption capability, etc. [1–3]. Nevertheless, B_4C possesses strong covalent-bonding, low plasticity, high resistance to grain boundary sliding and low superficial tension in the solid state. Otherwise, the presence of B_2O_3 on the surface of B_4C particle slows down the densification process [4]. All these factors make densification of powders difficult by conventional sintering and restrict the wide range of applications [5].

Therefore, many efforts have been devoted to improve the sinterability of B_4C in the last two decades [6,7]. In this context, the introduction of appropriate amounts of alumina to B_4C matrix is well known to overcome the drawbacks mentioned above [8,9]. Thus, several kinds of bulk ceramic composites in the B_4C–Al_2O_3 system have been investigated by various researchers using different fabricating routes [10–12]. But for conventional methods, temperature levels equal to or above 2100 °C are required for achieving adequate densification levels during pressureless sintering of B_4C/Al_2O_3 composites [11].

The latest one, often indicated as Spark Plasma Sintering (SPS), is a considerably novel technology where the powders and the die containing them are crossed by a pulsed electric current and simultaneously subjected to a mechanical pressure [13]. In graphite die, the punches transfer the pulsed current whose effects are not limited to Joule heating to the powder. Other non-thermal effects such as current enhanced mass transport, electroplasticity, and reactivity [14–17] have been identified. The applied pressure indirectly aids in the densification process by increasing the surface energy driving force. Furthermore, in comparison to hot-pressing sintering (HP), the higher heating rates and shorter dwell times during SPS process typically lead to products with finer microstructure, as a consequence of more favorable sintering conditions which avoid grain coarsening [18]. Fan et al. studied the effect of addition of alumina on the sinterability of boron carbide prepared by SPS at 1900 °C [19]. However, they believed the improvement of sintering character was attributed to the melting of Al_2O_3 additive near its melting temperature.

In the present study, the fabrication of dense B_4C/Al_2O_3 composites by spark plasma sintering at lower temperature

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(1750 °C) was achieved for the first time. The effects of Al_2O_3 additive on the densification behavior and microstructure of obtained B_4C ceramic have been investigated. Moreover, the formation of $AlB_{12}C_2$ as well as its formation temperature during SPS process was identified.

2. Experimental procedure

Commercially available B_4C powder (W5, Mudanjiang Boron Carbide Co., PR China) and Al_2O_3 powder (99.99% purity, particle size ≈2.4 μm, PR China) were used as raw material. The B_4C powder has a B:C ratio of 3:9, an average particle size of 5 μm and an oxygen content of 1.7 wt%.

The powder of Al_2O_3 was added to B_4C powder to give 0–12 wt% additive mixtures. Blending of starting powders was carried out by ball milling using a stainless steel jar with media made up of stainless steel balls and methanol for 3 h. After ball milling, the mixture was dried in a rotary vacuum evaporator at 70 °C and then placed in an aeration cabinet at 90 °C for 24 h. Pelleting of mixed powder was achieved by passing it through a 300-mesh screen. Eight kinds of specimens containing different amounts of Al_2O_3 were prepared, as listed in Table 1.

Spark plasma sintering was carried out in an SPS apparatus (SPS-3.2-MK-V, Sumitomo Coal Mining Co., Japan) using a graphite die with an inner diameter of 10 mm. The temperature was controlled by an optical pyrometer focused on the non-through hole located on the surface of the graphite die. The sintering experiments were conducted in vacuum atmosphere at different temperatures in the range of 1700–1800 °C with a dwelling time of 6 min under a pressure of 35 MPa. The heating and cooling rates were both 100 °C/min. To protect the die/plunger and make sample release easier after sintering, a molybdenum foil (0.15 mm thick, Sunstone, PR China) was inserted between the internal surface of the die and the sample as well as between its top/bottom surface and the plungers. Heat losses by thermal radiation were limited by covering the die with a 20 mm-thick graphite felt.

Table 1
Composition, sintering temperature and relative densities of B_4C matrix ceramics.

Al_2O_3 (wt%)	Sintering temperature (°C)	Relative density (%)
0	1700	72.86
	1750	74.49
	1800	76.97
1	1700	86.73
	1750	89.70
	1800	90.24
2	1700	91.98
	1750	96.33
	1800	95.46
4	1700	95.91
	1750	98.82
	1800	97.72
6	1700	96.10
	1750	98.29
	1800	96.38
8	1700	96.27
	1750	97.94
	1800	95.43
10	1700	93.51
	1750	97.92
	1800	95.28
12	1700	92.46
	1750	96.88
	1800	95.10

Densities of the consolidated specimens were measured using the Archimedes method with distilled water as the immersion medium. The phases were characterized by X-ray diffractometry (X'Pert PRO MPD, PANalytical, Netherlands) with Cu Kα radiation operated at 40 kV and 40 mA. The scanning speed was 5 °/min with a scan step of 0.0330°. The microstructure was observed under a scanning electron microscope (SEM) (S-4800, Hitachi-hitec, Japan) and chemical composition was qualitatively determined by an energy-dispersive spectrometer (EDS). Hardness test was performed by a Rockwell indentor with a load of 60 kg (HRA).

3. Results and discussion

3.1. X-ray diffraction

Fig. 1 shows the XRD patterns of the unmilled B_4C specimen (a) and the mixed powder of B_4C and Al_2O_3 (b). For pure B_4C, free carbon phase and B_2O_3 phase are detected besides B_4C phase according to the lower pattern in Fig. 1(a). As presented in the upper pattern, after the SPS process takes place, the diffraction peaks associated with free carbon have reduced significantly and no trace of B_2O_3 is found, which indicates that some carbon might react with B_2O_3 to generate B_4C [20]

$$2B_2O_3 + 7C \rightarrow B_4C + 6CO \quad (1)$$

When Al_2O_3 is added, four fundamental crystallographic phases are detected: B_4C, Al_2O_3, C and B_2O_3 as shown in Fig. 1(b).

Fig. 2 shows the X-ray diffraction patterns from B_4C composite ceramics with different Al_2O_3 contents sintered at 1700 °C, 1750 °C and 1800 °C. Similar to the specimen without alumina, B_2O_3 is not observed. A new phase, $AlB_{12}C_2$, is detected, which suggests that the reaction of B_4C, Al_2O_3 and C has taken place during the sintering. The reaction is as follows [21]:

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

According to Fig. 2, the concentration of $AlB_{12}C_2$ increases alone with the increase of Al_2O_3 addition. And one can easily find the residue of alumina and graphite which is considered to be the unreacted reactant.

3.2. Microstructure

The microstructure evolution of the samples was analyzed by SEM observations. The limited sintering for pure B_4C mentioned previously can be appreciated from the micrographs illustrated in

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