ARTICLE IN PRESS

Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Microstructure and properties of a graphene platelets toughened boron carbide composite ceramic by spark plasma sintering

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ARTICLE INFO

Keywords:
B_4C ceramic
Graphene platelets
Mechanical properties
Toughening mechanisms
Spark plasma sintering

ABSTRACT

A kind of B_4C/SiC composite ceramic toughened by graphene platelets and Al was fabricated by spark plasma sintering. The effects of graphene platelets and Al on densification, microstructure and mechanical properties were studied. The sintering temperature was decreased about 125–300 °C with the addition of 3–10 wt% Al. Al can also improve fracture toughness but decrease hardness. The B_4C/SiC composite ceramic with 3 wt%Al and 1.5 wt% graphene platelets sintered at 1825 °C for 5 min had the optimal performances. It was fully densified, and the Vickers hardness and fracture toughness were 30.09 ± 0.39 GPa and 5.88 ± 0.49 MPa m$^{1/2}$, respectively. The fracture toughness was 25.6% higher than that of the composite without graphene platelets. The toughening mechanism of graphene platelets was also studied. Pulling-out of graphene platelets, crack deflection, bridging and branching contributed to the toughness enhancement of the B_4C-based ceramic.

1. Introduction

Boron carbide is an important superhard material with the hardness second only to diamond and cubic boron nitride. It also has some attractive performances, such as low density, high elastic modulus, good wear and corrosion resistance, neutron absorption and high temperature semiconductor properties [1–3]. For its excellent comprehensive performances, it is widely used in the fields of nuclear energy, national defense and machinery, such as neutron absorption material, bulletproof armour engine nozzle, machining tools [4–9].

Nowadays, the main methods of fabricating B_4C ceramics for industrialization are hot pressing sintering and pressureless sintering. The sintering temperature is extremely high and the holding time is very long, but it is still difficult to prepare the dense B_4C ceramics with excellent mechanical properties. Zhang et al. used B_4C, Si and graphite powders to fabricate B_4C/SiC composites by hot pressing. The sample with the density of 98.6% can be sintered with the heating rate of 3 °C/min at 1950 °C for 60 min [10]. Kobayashi fabricated B_4C composite ceramics containing CNTs and Al by hot-pressing sintering with the holding time of 1 h [11]. The fracture toughness of the composite was slightly improved to 3.10 MPa m$^{1/2}$. Compared to the conventional sintering methods, spark plasma sintering (SPS) is an advanced sintering method, it has advantages of higher heating rate, shorter holding time and higher efficiency, which can densify the materials within a short time [12]. These are beneficial to prepare dence materials with fine grains [13]. When preparing B_4C ceramics by SPS, the sintering temperature is 200–300 °C lower than conventional sintering methods, the heating rate is about 100–200 °C and the holding time is about 1–10 min [2,14]. In the spark plasma sintering process, surfaces of the powders are purified by external pulse and strong current, so the diffusivity of the powder is improved, moreover the applied pressure promotes the plastic flow of the material. Therefore, the materials can be densified under a lower applied pressure in a short time [15–18].

The application of B_4C ceramic is limited due to its poor densification and low fracture toughness (only 2.9–3.7 MPa m$^{1/2}$) [4,9]. During the last few years, various metal oxides, metal simple substance, carbon or carbide and boride, such as CNTs, Al, Ti, Mg, Al_2O_3, Si, SiC, TiB_2, B, C, were added to improve the densification and toughness [10,11,19–23]. Sun et al. [20] studied the effects of Al_2O_3 on the densification behavior, microstructure and mechanical properties of B_4C composites. It was concluded that the addition of Al_2O_3 and the use of SPS technology is beneficial for the densification of B_4C. Relative density of the B_4C ceramics with a small content of Al_2O_3 was close to 99% and the Rockwell hardness was 90.7 HRA when sintered at 1750 °C. Xu et al.[6] studied that B_4C ceramics with sintering additives CaF_2/Y_2O_3 could be well densified at low temperature by SPS. The results showed that the density of B_4C ceramics was up to 99.1% with 0.5–1 wt% CaF_2/Y_2O_3 at the temperature of 1700–1750 °C.

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https://doi.org/10.1016/j.ceramint.2018.05.188
Received 26 April 2018; Received in revised form 21 May 2018; Accepted 21 May 2018

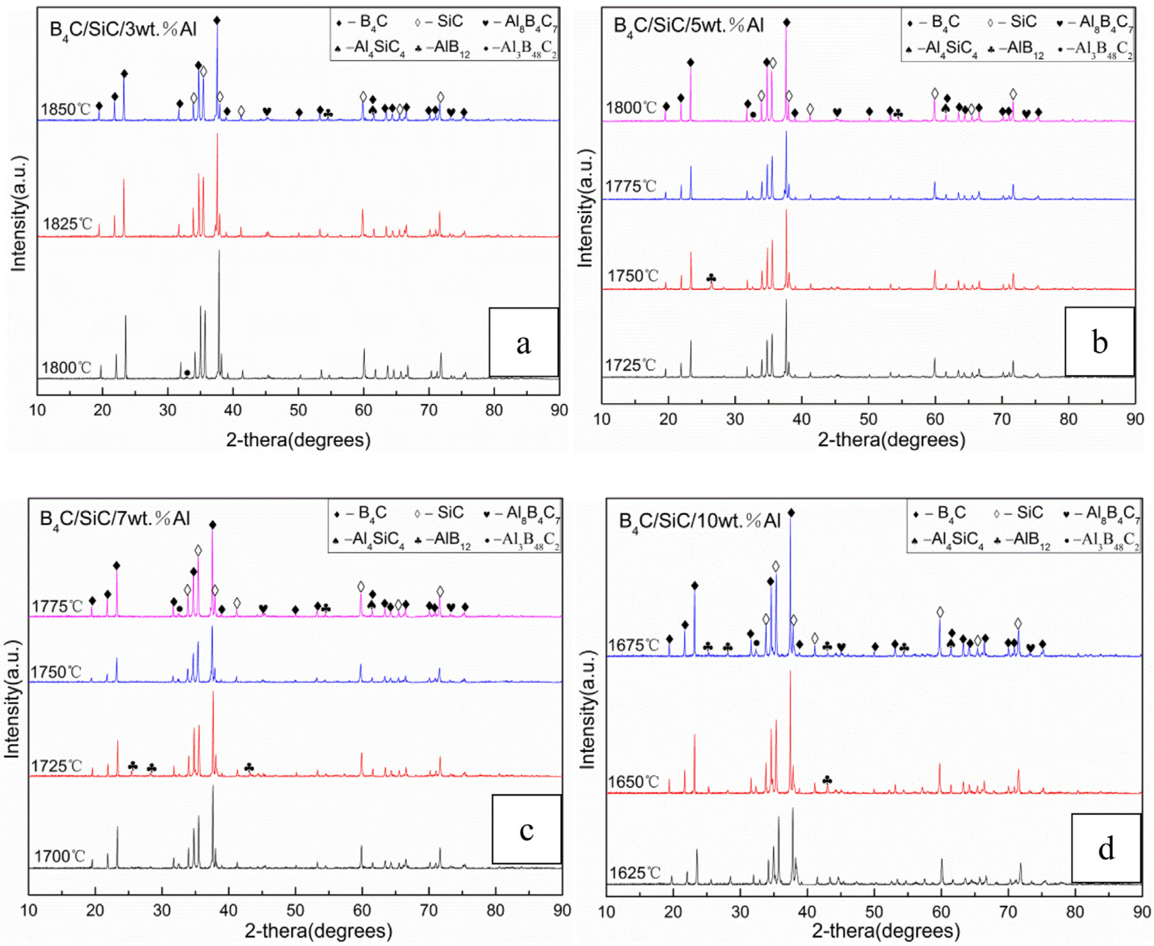

Fig. 1. The XRD patterns of (a) B_4C/SiC/3 wt%Al, (b)B_4C/SiC/5 wt%Al, (c) B_4C/SiC/7 wt%Al and (d) B_4C/SiC/10 wt%Al sintered at different temperatures.

Moshtaghioun et al. [21] prepared the B_4C/SiC and B_4C/SiC/C composites by SPS. The B_4C/15 wt%SiC composites with the density of 99.4% and the toughness of 5.7 MPa $m^{1/2}$ was fabricated at 1700 °C. It was found that the dispersed SiC grains could bridge the crack, which improved the toughness of B_4C ceramics. As a new type of carbon material, graphene platelets (GPLs) have unique two-dimensional structure and high tensile strength. As has been reported, they could enhance the fracture toughness, strength, tribological characteristics of ceramics, such as alumina, zirconium oxide and silicon nitride based ceramics [24–26]. Kovalčíková fabricated [9] B_4C ceramics with 4–10 wt% of GPLs by hot pressing at 2100 °C for 1 h. When GPLs was 4.5 wt%, the bending strength was 398 MPa and the fracture toughness was 5.89 MPa $m^{1/2}$. It was found that the overall mechanical properties would decrease but the fracture toughness would increase with the increase of GPLs content. Harshit et al. [27] studied GPLs reinforced Al_2O_3 ceramic composites prepared by SPS at 1350 °C. The results showed that the density of the composite was more than 99% and the fracture toughness increased to 3.9 MPa $m^{1/2}$, but the hardness slightly decreased as graphene platelets content increased. In the reported papers, there are many problems in fabricating B_4C, such as poor densification and low fracture toughness. The main problem is that the high hardness and high toughness could not be obtained simultaneously. The density and toughness of B_4C increase by adding toughening phases while the hardness decreases.

At present, searching for appropriate additives and sintering methods is of great significance to improve the mechanical properties of B_4C ceramic. Al could promote the densification of B_4C. GPLs are considered as an effective additive to enhance the toughness of ceramics. However, synergistically adding Al and GPLs into B_4C ceramic to improve its properties was rarely studied. In this paper, Al and GPLs were selected as the additives, and we attempted to prepare a fully densified B_4C ceramic material with high properties by SPS. The effects of additives and sintering temperature on densification behavior, mechanical properties and microstructure of B_4C ceramic were studied. The toughening mechanisms of GPLs were also investigated.

2. Experimental procedures

2.1. Preparation of B_4C-based ceramics

The B_4C/SiC/Al/GPLs (BSAG) composite ceramics were prepared using commercial powders: B_4C (1 μm, 99.9% purity), SiC (1 μm, 99.9% purity), Al (1 μm, 99% purity) and graphene platelets (GPLs, 30–50 nm, 96% purity). The raw powders were dispersed by ultrasonic vibration and mechanical stirring (DSA200-JY1-9.0L, China) for two hours. Then, the mixed powders were dried in a vacuum drying oven (Model DZF), and sieved through a 100-mesh sieve. The dried powders were packed into a graphite die with an inner diameter of 20 mm, which was pre-pressed with the pressure of 10 MPa for 5 min. The green compacts were sintered in a spark plasma sintering furnace (Model LABOX™-650, Japan) with a uniaxial load of 30 MPa in a vacuum. The heating rate was about 100 °C/min, and the sintering temperature was 1625–1850 °C with the holding time of 5 min.

2.2. Characterization

The relative density of the sintered samples was calculated by the Archimedes' method with the distilled water as the immersion media.