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Short communication

Ultra-fast densification of boron carbide ceramics under high heating rate and high pressure

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Abstract

Boron carbide ceramics were obtained in 2 min by a method based on self-propagating high-temperature synthesis plus quick pressing (SHS/QP). The samples were densified to 98% of theoretical density under a large mechanical pressure (120 MPa) and a fast heating rate (2300 °C/min). The microstructure and mechanical properties were studied. The sample obtained at this heating rate presents an average grain size of 3 μm and a hardness of 34 ± 0.2 GPa.

Keywords: C. Hardness; Ceramics; Boron carbide; Fast densification

1. Introduction

Boron carbide (B_4C) has been widely used as one of the most important and promising engineering ceramics due to its excellent physical and chemical properties, such as, low density ($\rho_v = 2.52$ g/cm^3), super hardness, high elasticity modulus, good wear and corrosion resistance, and neutron absorption ability [1]. Due to the presence of high fraction of strong covalent bonding, low plasticity and high resistance to grain-boundary sliding, densification of B_4C is difficult. Many efforts have focused on the preparation of dense B_4C by various sintering techniques [1–5]. In past work, there were two effective method help to obtain dense B_4C ceramics, the first method was increase sintering temperature, Roy employed pressureless sintering at 2375 °C to obtain samples whose densities were 93% of the theoretical density, and the grain size was above 10 μm, which the mean size of start powders was 0.8 μm [4], Thevenot found that the relative density of sintered B_4C could reach 90% by hot-pressing sintering at 1900 °C [6]. The second method was adding sintering aid. Some additives, such as Al_2O_3, Al, TiO_2 and AlF_3 can lower the densification temperature [7–9]. Kim obtained full dense B_4C ceramics with the addition of Al_2O_3 by hot-pressing sintering at 2000 °C, the grain size of sample was above 5 μm [10]. Although these additives were proved to be able to improve the densification and refine microstructure of B_4C ceramics, they might also result in the formation of grain-boundary phases and thereby influenced the mechanical behaviors of B_4C [1]. Subramanian et al. reported the hardness value of 30 GPa with the addition of ZrO_2 by pressureless sintering at 2275 °C [11]. A hardness value of 20–23 GPa with the addition of SiC was covered by Zorzi [12]. Goldstein also had gained full dense B_4C–ZrB_2 composite with hardness of 30–33 GPa by pressureless sintering at 2160 °C [13].

In this paper, a fast fabrication technique utilizing a very high heating rate and high pressure was developed. The heat generated by combustion reaction or self-propagating high-temperature synthesis (SHS) was applied to act as high-temperature source. A B_4C compact was loaded inside the combustion reactants. The whole reaction system was put into a steel die. A large mechanical pressure was applied, when the sample's temperature reached the maximum. Compared with other fabrication techniques, this method has advantages of higher heating rate (2300 °C/min), shorter densification time and larger pressure (120 MPa), which is predicted to refine the microstructure and enhance the densification. With such an

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approach, densification of B_4C ceramic can be obtained within 2 min.

2. Experimental procedure

The starting materials were high purity B_4C powders (Grade HS, H.C. Starck, Germany) with an average particle size of 0.7 μm. Three grams of powders was uniaxially pressed in a steel die into disks with a diameter of 12 mm and a height of 3 mm. The disk was followed by cold isostatic pressing (CIP) at 180 MPa.

A SHS reaction with high exothermic heat was shown as follows:

$$Ti + C \rightarrow TiC \quad (1)$$

The Ti (particle size <45 μm, 99% purity, BAODE Powder Metallurgy Co., Xi'an, China) and C (particle size <2 μm, 99% purity, Wuhan, China) powders (300 g) were mixed in a molar ratio of 1:1. After dried, the reactant mixtures with B_4C in the center were pressed into a cylindrical of 70 mm in diameter and 50 mm in height. The B_4C body was covered by a thin sheet of graphite foil to separate the B_4C from the reactants. The combustion and pressing process were carried out in a home-made instrument as shown in Fig. 1.

The 70 mm diameter reactants were placed in a steel die. Fully dried sands were placed between the sample and the die, which protect the die and transform the mechanical pressing force to the sample in a pseudo-isostatic manner. The SHS reaction was ignited by a tungsten coil galvanized with a short electrical pulse. The temperature of the B_4C was measured by a WRe5/26 type thermocouple and the maximum temperature of 2357 °C was measured. The temperature curve depending on time was shown in Fig. 2. This process has high heating rate (2300 °C/min). When the temperature reached the maximum, a quick hydraulic pressing was applied upon the sample. The applied mechanical pressure was in the range from 30 to 120 MPa. The pressing kept for 2 min and then was released, and the sample was allowed to cool naturally.

After sintering, The B_4C surface was polished, and the density was measured by Archimedes method. The microstructure was investigated by scanning electron microscopy (SEM, Hitachi-S3400N), after being polished and electrically etched. The grain size was measured from the SEM micrographs by the intercept method, in which the numbers of measured grains were about 150. The phase identification was characterized by XRD using a rotating anode X-ray

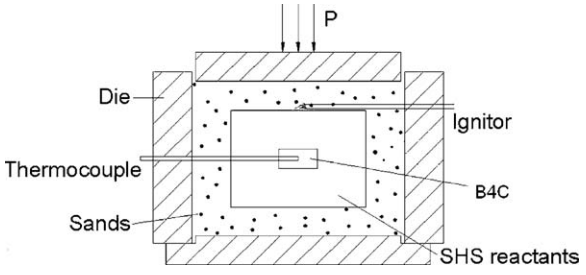

Fig. 1. Schematic representation of experiment process.

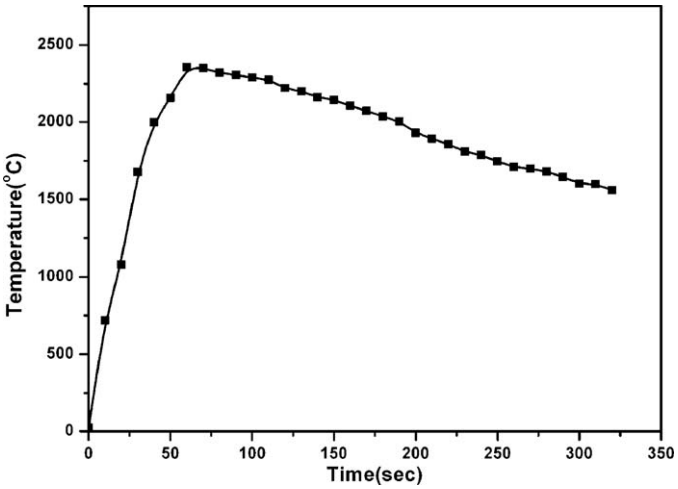

Fig. 2. Temperature curve vs. time during combustion process.

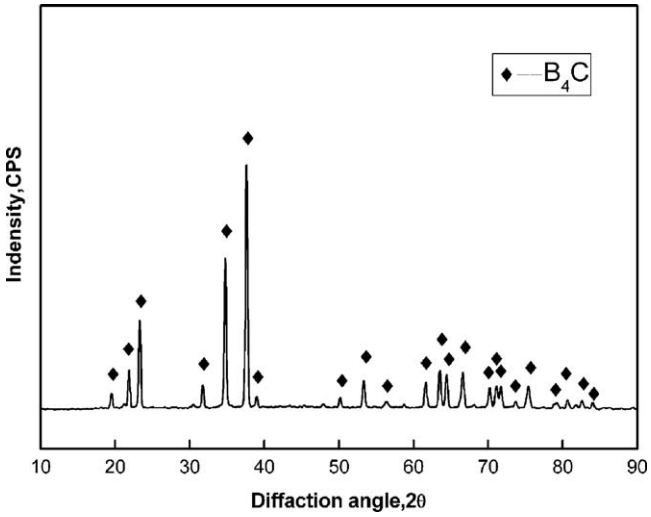

Fig. 3. X-ray diffraction patterns of the polished sample's surface

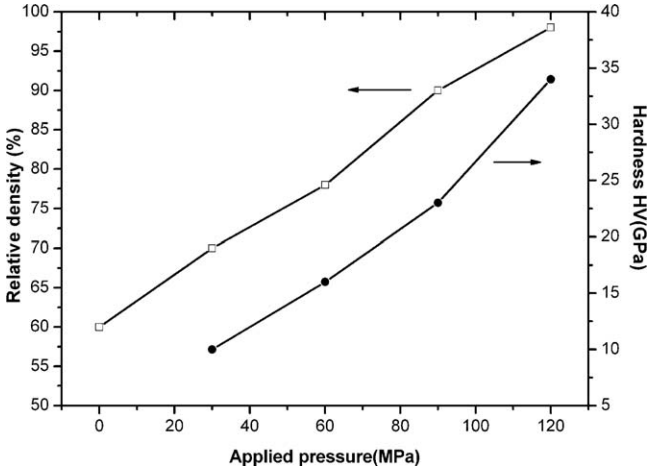

Fig. 4. Effects of applied pressure on the hardness and the relative density of the specimen.

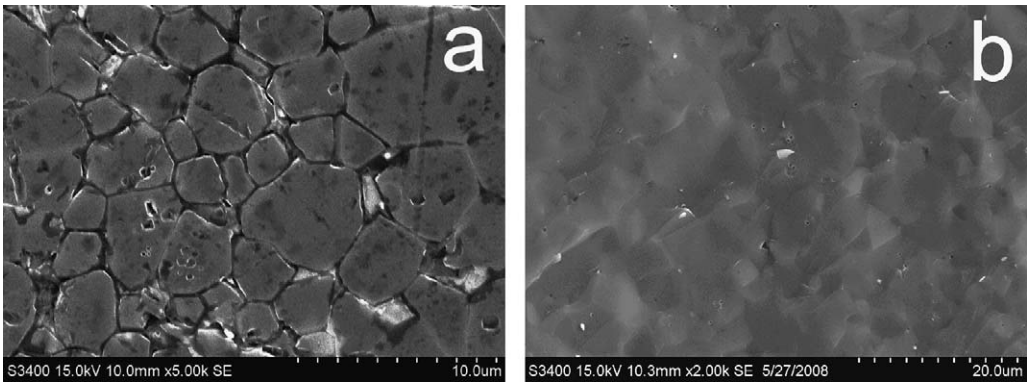

Fig. 5. SEM micrograph of the surface of sintered specimens under 120 MPa pressure (a. surface; b. fracture).

diffraction (Ultima III, Rigaku, and Japan). Vickers hardness measurements were carried out by the hardness testing machine (Wolpert 430SVD, USA) with a 5 kg load and 15 s dwell time.

3. Results and discussion

Fig. 3 shows the XRD patterns of the sintered specimens. In the sintered specimen spectra, there only consisted of the B_4C phase and no impurity phase was detected. It is implied that the combustion reaction has no contamination on the sintered samples. When the SHS reaction takes place, the temperature rises rapidly and a large amount of gas generated, which forms a great and outward pressure, and prevents the contamination form the B_4C sample.

Fig. 4 shows the effect of mechanical pressure on relative densities and hardness of B_4C samples. When the mechanical pressure increases from 0 to 120 MPa, the relative densities of B_4C samples increased from 60 to 98%. The mechanical pressure is helpful to remove pores from the powder compact and provides additional driving force for densification. The Vickers hardness of B_4C increases as mechanical pressure increases. The Vickers hardness reaches 34 GPa under the pressure of 120 MPa, which is higher than previous reported results.

Both porosity and grain size influence the hardness and strength of polycrystalline B_4C, according to Eq. (2) [14]:

$$H = -40.98 + \left(\frac{8.00}{G^{0.35}}\right) + 51.26(1-P)^2 \quad (2)$$

Here H is hardness; G is grain size; P is porosity. The increase in hardness can be attributed to small grain size and high density. Typical SEM images of the densified B_4C specimen at 120 MPa are shown in Fig. 5. A very small number of voids are observed. The average grain size is about 3 μm (ranging from 1 to 6 μm), compared with the raw powders particle size, the grain size of densification B_4C grown only four times form Fig. 5(a). Fig. 5(b) shows SEM micrographs of fracture surfaces of the B_4C specimen. The intragranular fracture mode is dominant during fracture, indicating the presence of strong grain-boundaries and leading to a high measured strength.

4. Conclusions

The B_4C was densified by the heat from SHS with a heating rate of 2300 °C/min, and the mechanical pressure of 120 MPa in 2 min. The maximum hardness of the dense B_4C specimen is 34 ± 0.2 GPa. This method has higher heating rate and shorter sintering time than traditional sintering process, which leads to maximal temperature and minimal grains coarsening.

Acknowledgements

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