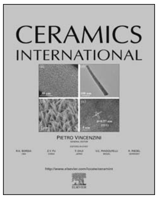
ARTICLE IN PRESS

Ceramics International (xxxx) xxxx–xxxx

Contents lists available at ScienceDirect

Ceramics International

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



Effects of pressure on densification behaviour, microstructures and mechanical properties of boron carbide ceramics fabricated by hot pressing

Xiaorong Zhang[a], Hongjun Gao[b], Zhixiao Zhang[c,*], Ruolin Wen[c], Guangsuo Wang[c], Jingbo Mu[c], Hongwei Che[c], Xiaoliang Zhang[c]

[a] *College of Mechanical and Equipment Engineering, Hebei University of Engineering, Handan 056038, China*
[b] *College of Civil Engineering, Hebei University of Engineering, Handan 056038, China*
[c] *College of Materials Science and Engineering, Hebei University of Engineering, Handan 056038, China*

ARTICLE INFO

Keywords:
Boron carbide
Hot pressing
Densification behaviour
Microstructure
Mechanical property

ABSTRACT

Effects of pressure, from ordinary (30 MPa) to high pressure (110 MPa), on densification behaviour, microstructures and mechanical properties of boron carbide ceramics sintered by hot pressing are investigated. With increasing pressure, the relative density sharply increases within 30–75 MPa, slowly increases within 75–100 MPa and finally stagnates. For samples within 75–100 MPa, densification begins at approximately 1000 °C, and the dominant densification process ends before the soaking stage. High relative densities of 98.49% and 99.76% are achieved. For samples within 30–50 MPa, densification begins at approximately 1500 °C, and the soaking stage (initial 20 min) is still important for the dominant densification process. The final relative densities are only 87.90% and 92.32%. The above-mentioned differences are derived from contributions of pressure, and the dominant densification mechanism under high pressure is plastic deformation. The average grain size of the samples slightly increases with increasing soaking time. The grain size under higher pressure is larger than that under lower pressure at corresponding periods because grains grow easily with reduced pores. Vickers hardness and fracture toughness increase as grain size decreases in fully dense samples. However, when the samples do not achieve full density, relative density becomes more influential than grain size in hardness and toughness. A soaking time of 30 min is enough for samples under 100 MPa. Prolonging the soaking time has deleterious effects on mechanical properties. The relative density, grain size, hardness and fracture toughness of the samples under 100 MPa for 30 min are 99.73%, 1.96 µm, 37.85 GPa and 3.94 MPa m$^{1/2}$, respectively.

1. Introduction

Boron carbide (B_4C) is a desirable material because of its outstanding physical and chemical properties, including high melting point, good wear resistance, excellent chemical stability and good neutron absorption capability [1–4]. These superior properties make B_4C a promising engineering material for structural parts. Most importantly, B_4C has low density (2.52 g/cm^{-3}) and is the third hardest material (after diamond and cubic boron nitride) under ambient conditions; it is the hardest material at temperatures higher than 1100 °C [5–7]. The unique combination of low density and high hardness makes B_4C an optimal candidate for special applications, such as lightweight armour and high temperature resistance wear parts [1,8]. However, densification of pure B_4C ceramics is difficult because of their low self-diffusion coefficient, which results from the strong covalent bonding between atoms, low plasticity, high resistance to grain boundary sliding and low surface tension in the solid state [9]. In addition, the fracture toughness of the B_4C ceramics is low, which is a non-negligible factor that hinders their further development and applications. Although addition of second phases, such as C, Al, SiC, TiB_2, Al_2O_3 and ZrB_2 [10–15], into the B_4C matrix is advisable to improve the sinterability and fracture toughness of B_4C ceramics, the second phase induced often has deleterious effects on hardness or lightweight property.

To maintain the unique feature of combined low density and high hardness for B_4C ceramics, researchers attempted to develop new techniques and methods to obtain dense pure B_4C ceramics. At present, pure B_4C has been fabricated using pressureless sintering [15–17], hot pressing [18–20], spark plasma sintering [21–23] and new ultra-fast densification technologies [24,25], such as self-propagating high temperature synthesis plus quick pressing (SHS/QP). Among these techniques, the density and properties of the products fabricated using

---

[*] Corresponding author.
E-mail address: zhixiao351@hebeu.edu.cn (Z. Zhang).

http://dx.doi.org/10.1016/j.ceramint.2017.02.043
Received 17 January 2017; Received in revised form 10 February 2017; Accepted 10 February 2017
0272-8842/

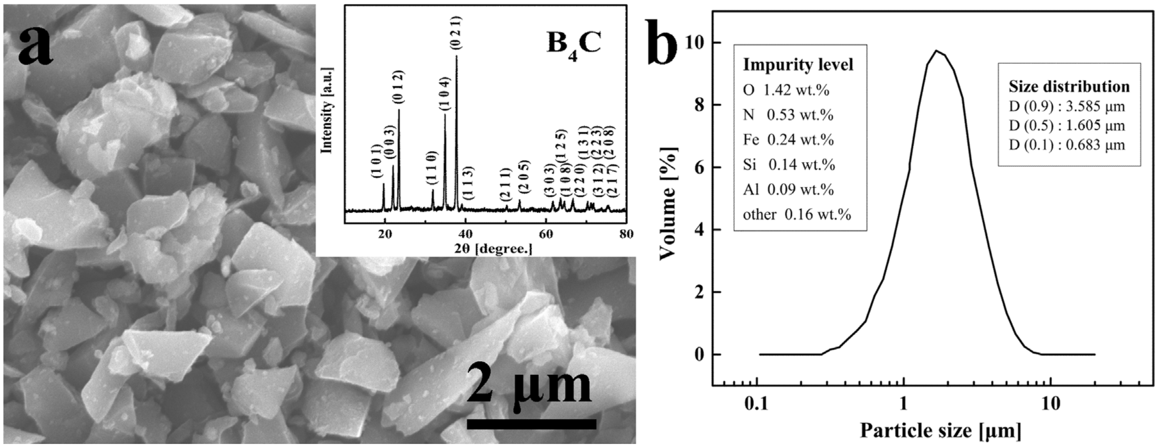


Fig. 1. Characteristics of B_4C powders. (a) SEM image and XRD pattern, and (b) particle size distribution and impurity level.

pressureless sintering are inferior even if the sintering temperature exceeds 2200 °C. Although relatively dense B_4C ceramics with fine grain size can be obtained by spark plasma sintering or SHS/QP, the fast heating rate and short holding time lead to an inhomogeneous structure between the interior and exterior of the samples. Therefore, the sample size fabricated via spark plasma sintering or SHS/QP is limited, i.e., usually less than 20 mm, and affects the industrial application of B_4C ceramics. By comparison, larger-sized samples with relatively high density can be fabricated by hot pressing due to slow heating rate, long soaking time and pressure. Therefore, hot pressing is a more reasonable fabrication process for B_4C ceramics.

By using ordinary hot pressing (20–50 MPa), pure B_4C ceramics with 94–98% theoretical density can typically be obtained within 2100–2300 °C for approximately 60 min [1]. However, deterioration of the mechanical properties of B_4C ceramics is inevitable because of grain coarsening at temperatures exceeding 2000 °C. The optimal properties of the B_4C ceramics cannot be achieved. Therefore, the method of fabricating dense pure B_4C ceramics with fine grain by hot pressing at temperatures lower than 2000 °C by optimising the sintering parameters should be studied. Related works have been performed. X Du *et al.* [26] studied the effects of particle size on densification and microstructure of B_4C ceramics. The diffusion activation energy decreases, but the relative density and the densification rate increase as mean particle size decreases. R Angers *et al.* [19] studied the effects of holding time, sintering temperature, heating rate and cooling rate on the sinterability of B_4C ceramics. The parameters have several effects on the densification of the B_4C ceramics, but the breakthrough in obtaining dense B_4C below 2000 °C has not been achieved by adjusting these parameters. In fact, pressure is also an important parameter. W Ji *et al.* [7] fabricated dense B_4C ceramics with no grain growth at 1750 °C through spark plasma sintering by increasing the pressure to 80 MPa and proved that plastic deformation was the dominant densification mechanism under high pressure. High pressures can effectively decrease sintering temperature, thereby restricting grain growth during spark plasma sintering. Similarly, the concept should be transplanted into the hot pressing technology. An optimised pressure level, especially high pressure (60–100 MPa), is expected to yield dense B_4C ceramics with fine grain sizes during hot pressing at temperatures lower than 2000 °C. However, the pressure applied in hot pressing is usually 20–50 MPa for B_4C ceramics. Fabricating dense B_4C samples by applying high pressure (60–100 MPa) has been infrequently studied. Moreover, studies on the effects of pressure, from ordinary pressure (30 MPa) to high pressure (100 MPa), on the characteristics of B_4C are few. Therefore, systematic studies on the effects of pressure on the densification, grain size and mechanical properties of the B_4C ceramics are necessary for hot pressing.

Effects of ordinary (30 MPa) to high pressure (110 MPa) on densification, microstructures and mechanical properties of the B_4C ceramics sintered by hot pressing were systematically studied in the present work. Densification behaviour of the B_4C ceramics under different pressure was analysed through densification curves and densification rate curves. The dominant densification mechanism under high pressure was discussed. The relationships among pressure, relative density, grain size and mechanical properties were explored. Finally, dense B_4C ceramics with little grain growth and superior mechanical properties were obtained at 1900 °C by hot pressing with high pressure (100 MPa).

2. Experimental procedure

2.1. Raw materials

Commercially available B_4C powder (97.5% purity, Mudanjiang Jinganzuan Boron carbide Co., Ltd., China) was used as the starting material. The morphology, phase composition, particle size distribution and impurity level of the powder are shown in Fig. 1.

2.2. Hot pressing procedure

B_4C ceramics were sintered by a hot-pressing sintering apparatus (916 G-G Press, Thermal Technology LLC, USA). B_4C powders sieved using 200 mesh grids were placed in a cylindrical graphite die with an inner diameter of 30 mm. The cylindrical graphite die was machined from commercially available high-strength graphite (ISO-68, Shanghai toyotanso Co., Ltd., China) whose compression strength overs 170 MPa at ambient temperature and 120 MPa at high temperature (2000 °C). The density of the graphite is 1.82 g/cm^3. The interior of the die and the surfaces of punches were covered with 0.2-mm-thick graphite foil. A thin protective layer of boron nitride was coated on the inner surfaces of the graphite foils to reduce the friction between movable parts. The temperature was monitored by a thermocouple (below 1200 °C), and an infrared pyrometer (above 1200 °C) focused on the surface of the graphite die.

Equal amounts of B_4C powders (7.1 g) were used for each hot pressing. The powders were firstly heated under vacuum from room temperature to 1500 °C with the heating rate of 20 °C/min, and then continuously heated to sintering temperatures of 1900 °C with the constant heating rate of 10 °C/min under an argon atmosphere. The target pressures were achieved at 300 °C, and maintained during the rest of heating and soaking time during the hot pressing. Then, the samples were naturally cooled by turning off the power at the end of the soaking. Meanwhile, the pressure was removed. The selected ranges of pressure, sintering temperature and soaking time were 30–110 MPa,