Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 40 (2014) 4359–4366

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Densification behavior and related phenomena of spark plasma sintered boron carbide

Xiaoguang Li[a,b], Dongliang Jiang[a,*], Jingxian Zhang[a,*], Qingling Lin[a], Zhongming Chen[a], Zhengren Huang[a]

[a]State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China

[b]Graduate University of the Chinese Academy of Sciences, Beijing 100049, China

Received 18 June 2013; received in revised form 18 August 2013; accepted 26 August 2013
Available online 3 September 2013

Abstract

In this work, boron carbide ceramics were sintered in the temperature range of 1400–1600 °C by spark plasma sintering (SPS). The influence of sintering temperature, heating rate, and holding time on the microstructure, densification process and physical property was studied. The heating rate was found to have greater influence than that of the holding time on the microstructure and the densification of boron carbide. The optimal sintering temperature was 1600 °C under the heating rate higher than 100 °C/min. The relative density, flexural strength, Vickers hardness and fracture toughness of the sample synthesized at 1600 °C were 98.33%, 828 MPa, 31 GPa and 2.66 ± 0.29 MPa $m^{1/2}$, respectively. The densification mechanism was also investigated.

Keywords: Boron carbide; Spark plasma sintering; Sintering behavior; XRD; TEM

1. Introduction

Boron carbide was a covalently bonded compound with high melting point (2427 °C), a relative low density (2.52 g/cm^3), extremely high hardness (only after c-BN and diamond) and high neutron absorption cross-section [1]. It had been used for light weight armor, wear-resistant components and control rods in nuclear reactors due to the attractive properties [1,2]. Pressureless sintering method to get high density pure boron carbide had proved to be difficult. Pressure-assistant sintering methods (hot pressing (HP) or hot isostatic pressing (HIP)) had usually been employed to produce almost fully densified boron carbide ceramics [1,2]. The pressure was recognized to promote the densification by facilitating particle rearrangement, plastic deformation and pore elimination [3].

Spark plasma sintering (SPS) was a special sintering process by combination of uniaxial pressure and powerful DC pulsed current to consolidate materials [4–6]. SPS can be used to produce specimens with outstanding properties and limited grain growth at lower temperature within shorter heating time [4–7]. Abnormal grain growth usually occurred in pressureless sintered boron carbide, which resulted in the performance degradation. In addition, boron carbide was electro-conductive material, the applied pulsed current could possibly contribute to the densification process and result in the material with attractive properties [1]. Thus, SPS was a promising approach for the preparation of boron carbide with high performance.

SPS had been used to consolidate boron carbide ceramics [8–22]. In SPS sintering, pore free ceramics were usually fabricated by adding sintering aids (e.g. SiC, TiB_2) or through reaction sintering method [9,11–15,21,22]. Dense boron carbide ceramics prepared directly using only boron carbide powder were rarely reported [10,16–20]. Hayun et al. [16] fabricated dense pure boron carbide ceramics using boron carbide powder and studied the effect of sintering temperature, holding time, applied pressure and heating rate on the sintering

*Corresponding author at: No. 1295 Dingxi Road, Channing District, Shanghai 200050, China.
Tel.: +86 21 52412167; fax: +86 21 52413122.
E-mail addresses: dljiang@mail.sic.ac.cn (D. Jiang), jxzhang@mail.sic.ac.cn (J. Zhang).

0272-8842/$ - see front matter © 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2013.08.106

behavior of boron carbide ceramics in the temperature range of 1800–2200 °C. It was found that the relative density increased with the increase of sintering temperature, holding time and applied pressure. Boron carbide with finely equiaxed grains and homogeneous microstructure can only be obtained at high sintering temperature of 2200 °C with very high heating rate (600 °C/min). It was also found that the impurities possibly improved the densification at the early stage of sintering by forming liquid phase. Moshtaghioun et al. [10] explored other factors influencing the sintering behavior of boron carbide. Results showed that the powder size is an important factor that influences the sintering temperature. The densification mechanism was not referred in the literature.

In the present work, boron carbide ceramics with high performance were fabricated without employing sintering additives. The effect of sintering temperature, heating rate and holding time at different sintering temperatures on the densification and microstructure was studied in the temperature range of 1400–1600 °C. Moreover, the densification mechanism of SPS sintered boron carbide was also deeply investigated.

2. Experimental procedure

Commercially available boron carbide powder (Mudanjiang Jingangzuan boron carbide Co. Ltd., Mudanjiang, China) with the mean particle size of 493.8 nm was used as the starting powder. To reduce the impurity content, the as-received powder was firstly dispersed in dilute HCl solutions and then washed with deionized water. After drying at 100 °C for 2 h, the powder was sieved using 200 mesh grids. The as-treated powder was then filled into a cylindrical graphite die with the inside/outside diameter and height of 20 mm/50 mm and 40 mm, respectively. Two graphite discs of 20 mm diameter were placed on the top and bottom of the sample. Graphite paper was also rolled and placed on the inner surface of die before the boron carbide powder was filled in. A SPS system (SPS 2040, Sumitomo Heavy Industries Ltd., Japan) was used to consolidate the boron carbide powder. The pulse cycle of the DC current was 12:2 (i.e., twelve 3 ms pulses on and two 3 ms pulses off). The DC current flowed from top punch down toward bottom punch, while the pressure was applied along the opposite direction. After sintering, the disc shaped sample was cut into bar-shaped sample of 2 mm × 4 mm × 18 mm in size.

The three-point flexural strength measurement was performed using a universal testing machine (Mold 5566, Instron, America) with a span of 12 mm. Vickers hardness was determined using a hardness tester (Wilson–Wolpert Tukon 2100B, America) with 1 kg load on polished surface. The fracture toughness was also measured in the hardness testing machine by the indentation method. The density of sample was measured using Archimedes' method. The phase composition of the sample was determined by X-ray diffraction (XRD, D/max 2550V, Rigaku, Japan). The microstructure of sample was observed using a scanning electron microscopy (SEM, TM-1000, Hitachi, Japan) and a transmission electron microscopy (TEM, JEM-2100F/200F, Joel, Japan) with an energy dispersive X-ray spectrometer attachment (INCA, Oxford instruments, Britain). To determine the grain size of boron carbide ceramics, the specimens were polished and etched in dilute KOH solutions under DC current of 0.02 A for 30–60 s using a DC current equipment (LW15J2, Shanghai Liyou, China). The mean grain size was determined from SEM micrograph, and at least 300 grains were measured to get the statistical mean size.

3. Results and discussion

3.1. Densification

The relative density of boron carbide ceramics sintered at different temperatures under the heating rate of 100 °C/min and the holding time of 3 min was shown in Fig. 1. The density noticeably increased with the increase of the temperature up to 1500 °C, and then kept almost constant thereafter in the temperature range of 1500–1600 °C. The densities of boron carbide ceramics were 65.39% and 75.17% after sintering at 1400 °C and 1450 °C (Fig. 1), respectively. High relative density over 95% was achieved when the temperature was above 1500 °C. The relative density of 98.32% can be reached at 1600 °C (Fig. 1). A increase in density from 92–93% to 99% had ever been observed when the SPS sintering of pure boron carbide was carried out from 1650 °C to 1750 °C [10]. However, the reason for density increase was not discussed in the literature. The abrupt increasing of relative density from about 60% at 1600 °C to 95% at 1675 °C was observed in SPS-reaction-sintered SiC [23,24], which was related to the disorder-to-order transformation and accompanied by mass transport in this temperature range. In our case, a different mechanism will be reasonably proposed for the increase in density, which would be discussed in following section.

The microstructure of the samples under different sintering temperature was shown in Fig. 2. No any obvious grain growth was observed at 1400 °C as shown in Fig. 2(a). At 1450 °C (Fig. 2(b)), sintering necks appeared while the compact was still in interconnected porous structure. Though the most part

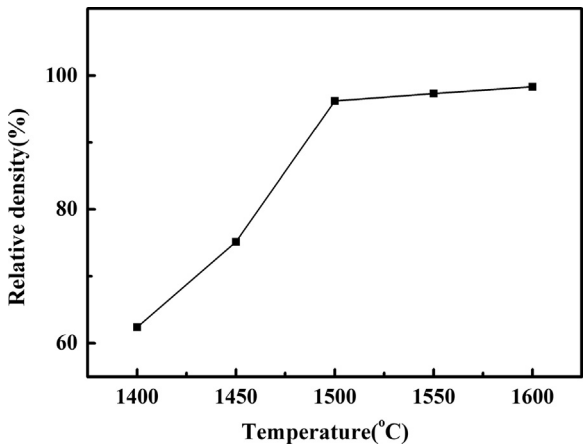

Fig. 1. Relative densities of boron carbide ceramics sintered at 1400 °C, 1450 °C, 1500 °C, 1550 °C and 1600 °C for 3 min under the heating rate of 100 °C/min.