Available online at www.sciencedirect.com
SciVerse ScienceDirect
Ceramics International 39 (2013) 2123–2126
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Short communication

Aqueous tape casting of boron carbide ceramic

Zhaohua Luo[a,b], Zhihui Lv[a,b], Dongliang Jiang[a,*], Jingxian Zhang[a], Zhongming Chen[a], Zhengren Huang[a]

[a]*State Key Laboratory of High Performance Ceramics and Superfine Microstructures, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China*
[b]*Graduate University of the Chinese Academy of Sciences, Beijing 100049, China*

Received 11 July 2012; accepted 16 July 2012
Available online 23 July 2012

Abstract

An environmental friendly aqueous tape casting process has been introduced to fabricate B_4C green tapes. Tetramethylammonium hydroxide (TMAH) and a mixture of waterborne epoxy emulsions and anionic aliphatic urethanes emulsions were selected as the dispersant and binder, respectively. The influence of pH value on the zeta potential of ceramic suspensions has been investigated, and the dispersant content added has been optimized based on the rheological behaviors of B_4C slurries. The green sheets showed homogeneous microstructure with high flexibility and enough strength for the subsequent cutting and lamination. After sintering at 2100 °C, dense B_4C ceramics can be achieved. The relative density and the flexural strength of the sintered samples were 96.8% and 636 ± 70 MPa, respectively.

Keywords: A. Tape casting; C. Mechanical properties; D. Carbides

1. Introduction

It is widely acknowledged that boron carbide ceramics are formed with strong covalent C–B and B–B bonds which gives them some superior properties, such as extremely high hardness (Vickers: 3770 kg/ mm^2), good erosion behavior, high wear resistance and melting point, plus with low density (2.52 g/ cm^3) and high neutron absorption cross section [1–5]. Benefit from these excellent mechanical and chemical performances, B_4C ceramics has received much interest in industrial and other applications. For example, B_4C ceramics cannot only be used as abrasive grit, sand-blasting nozzles and high temperature thermoelectric conversion material, but also can be used as light-weight armor plates or a neutron absorber in nuclear reactors [4,6].

So far, the fabrication of the green preforms of B_4C ceramics were mainly focused on the die pressing and slip casting method, and only a few researchers took the gel casting, strong magnetic field and tape casting techniques [7–11]. Among them, tape casting is an interesting, effective and readily established method to produce flat ceramic substrates with homogeneous microstructure in electronic industry and structural ceramics preparation, and its biggest advantage lies especially in fields need multilayer or gradient structures [12–14]. According to the solvent nature of the slurry, tape casting can be divided into non-aqueous and aqueous tape casting, respectively. Though the former one has the advantage of easy and fast evaporation of solvent which is important in continuous casting process, aqueous tape casting has received more and more attention because of its environmental friendly and cost effective features [15,16]. In both cases, however, stable and well dispersed slurry with the possible high solid content and desired viscosity in tape casting processes is an insurance to achieve green tapes with uniform, smooth structure and high density [17]. Unfortunately, preparation of B_4C green tapes by tape casting technology was just focused on the non-aqueous one [11].

The major aim of the present study was to fabricate B_4C ceramics by aqueous tape casting method. The rheological

*Corresponding author at: Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China.
Tel.: +86 21 52412606; fax: +86 21 52413122.
E-mail address: dljiang@mail.sic.ac.cn (D.L. Jiang).

0272-8842/$ - see front matter
http://dx.doi.org/10.1016/j.ceramint.2012.07.048

behaviors of aqueous slurries with different dispersant contents and solid contents were first investigated, and then the microstructure and mechanical properties of the green tapes and as sintered B_4C ceramics were also studied.

2. Experimental procedure

The starting B_4C powders (average particle size as 0.52 μm and a specific surface area as 7.89 m^2/ g, C, 20.52 wt%; B, 77.34 wt%; O, 0.72 wt%) involved in the fabrication of green tapes were commercially available. Tetramethylammonium hydroxide (TMAH, supplied as a 25 wt% water solution, Shanghai Chemical Reagents Co., China) was selected as dispersant. The mixture of water-borne epoxy emulsions GEM02 (50 wt%, pH: 6–8) and anionic aliphatic urethanes emulsions Impranil LP RSC 1554 (60 wt%, pH: 6.8–8.5) with the mass ratios as 2:1 were used as the binder, and the whole content of binder was 18 wt%.

Before the preparation of aqueous slurries, B_4C powders were first handled by acid treatment to remove the impurities, especially the B_2O_3 on the particles surfaces which would be detrimental to the B_4C ceramics sintering [5,18]. Then, the dispersant and as-treated B_4C powders were added into the distilled water sequentially, followed by ball milling for 24 h. After that, the binder was added into the slurries and ball milled for another 24 h. Next, slurries were degassed in vacuum condition to remove gas bubbles in them. The tape casting was performed on a Procast Precision Tape Casting Equipment (Division of the International, Inc., Ringoes, NJ) with a gap height of 400 μm and a carrier film speed of 100 mm/min, respectively. After drying in air for a few hours, the obtained B_4C tapes were laminated and heat treated at 600 °C for 1 h in vacuum to burn out the binder. Finally, the compacts were hot-pressed at 2000 °C and 2100 °C, respectively, for 30 min with the applied pressure of 35 MPa under a flowing argon atmosphere.

Zeta potential of the B_4C powder suspensions with or without dispersant at different pH conditions were measured with Zetaplus (Brookhaven Instruments Corp., USA). The rheological behavior at room temperature was measured using a rotating viscometer (Anton Paar PheolabQC, Austria).

The densities of the sintered samples were measured by Archimedean method. The three point flexural strength of the sintered specimens (by size of 3 mm × 4 mm × 36 mm) were tested on a material testing system (Model 5566, Instron Corp., UK) with the span width and crosshead speed of 20 mm and 0.5 mm/ min, respectively. The Vickers hardness and fracture toughness were calculated based on indentation test with a load of 50 N for 10 s on a Vickers hardness tester (Wilson-wolpert Tukon-2100B, Instron, Corp.). The microstructures of the cross section of the sintered B_4C ceramics were characterized by SEM (JSM-6700F, JEOL Ltd., Japan).

3. Results and discussion

The influence of pH value on the rheological properties of ceramic slurries was a key issue in aqueous tape casting process [19]. The zeta potential of the B_4C slurries with and without the addition of dispersant at different pH conditions were shown in Fig. 1. Owing to the fact that B_2O_3 layers were easily formed on the B_4C particle surfaces, the zeta potential of the powder was negative throughout the entire setting pH region. Moreover, in aqueous solution the TMAH can dissociate as the following equation [20]:

$$(CH_4)_4N(OH) \rightarrow (CH_4)_4N^+ + OH^-$$

As the addition of some amount of TMAH, the dissociated OH^- can promote the dissociation of the boron oxide and cause more negative charge on the B_4C particle surface which can be expressed as follows:

$$B_2O_3 \xrightarrow{2OH^-} 2[BO_2]^- + H_2O$$

On the other hand, the increased ionic strength in the suspension would compress the thickness of the double electric layer and lead to the significant increase of zeta potential of the B_4C particles. As a result, the presence of TMAH could help specifically with the increase of the repulsion force among particles and improve the suspension stability. In addition, it shows that the optimal pH should be in the range of 6–8. For concentrated slurries it was shown that the slurry pH was a bit higher around 9–10 for keeping high stability.

However, the dispersant content also has an effect on the dispersity of the ceramic slurries. Fig. 2 shows the viscosity of 45 vol% B_4C slurries as a function of shear rate with different TMAH contents. It can be observed that when the dispersant contents were relatively low, the rheological properties exhibited shear-thickening characteristics and it turned to the shear-thinning behaviors when the TMAH content exceeded 0.5 wt%. Additionally, it can be found that the viscosities of slurries at shear rate of

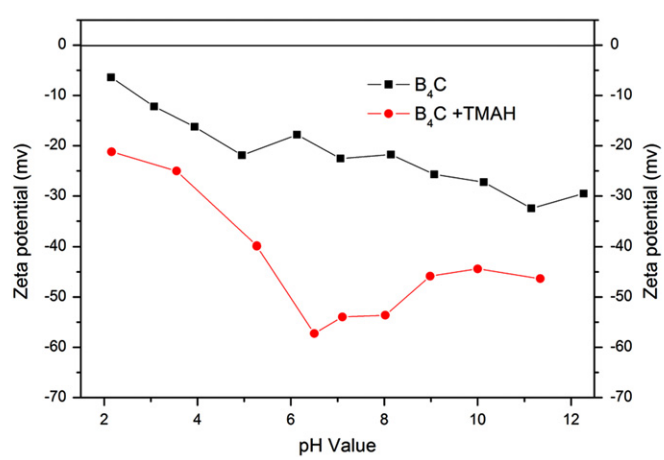

Fig. 1. Zeta potential of B_4C at the absence and presence of TMAH.

$100\ s^{-1}$ were 1.622 Pa s, 0.096 Pa s, 0.080 Pa s, 0.088 Pa s and 0.096 Pa s when the TMAH contents were 0.25 wt%, 0.4 wt%, 0.5 wt%, 0.6 wt% and 0.7 wt%, respectively. Though the viscosities did not vary so much, it can be concluded that the optimal dispersant contend would be 0.5 wt%. The excess amount of dispersant tended to form a bridging effect between separated particles and disturb the electrostatic force among ceramic particles [21].

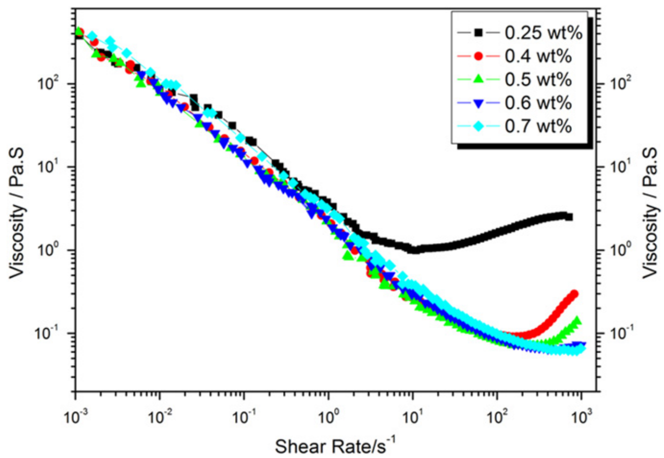

Fig. 2. Rheological curves for 45 vol% B_4C slurries with different contents of TMAH.

After tape casting process, smooth, complete and defect free B_4C green tapes could be obtained, and the tapes possessed good flexibility and machinability for free bending and clipping (Fig. 3a). In addition, the microstructure of the tape surface in Fig. 3b shows that the B_4C particles and pores were homogeneously distributed.

Table 1 lists the measured bulk densities and the mechanical properties of the sintered B_4C ceramics sintered at 2000 °C and 2100 °C, respectively. It is obviously showed that the B_4C ceramic could not be sintered well when the sintering temperature was 2000 °C while the relative density was 93.4% and there existed some conspicuous pores in the sintered samples (Fig. 4a). When sintered at 2100 °C, the performances of the B_4C ceramics were improved significantly, the relative density, flexural strength, Vickers hardness and fracture toughness achieved to 96.8%, 636 ± 70 MPa, 30.8 ± 0.6 GPa and 3.9 ± 0.1 GPa, respectively. Moreover, microstructure of the fracture surface in Fig. 4b shows that

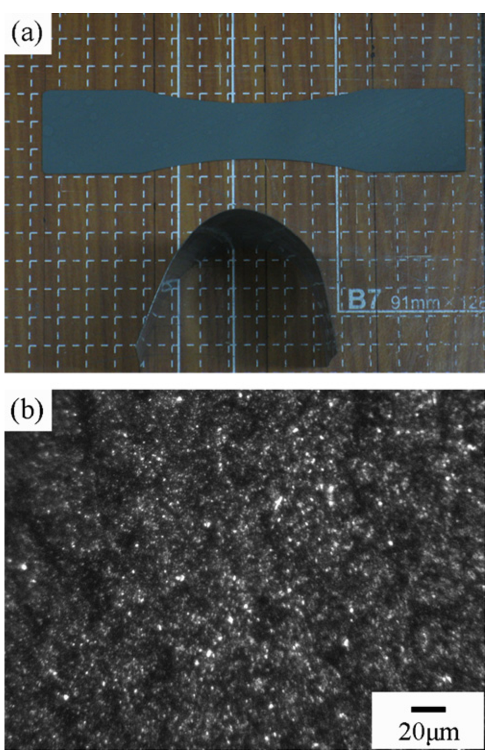

Fig. 3. The typical dried green tape (a) and the microstructure of the tape surface (b).

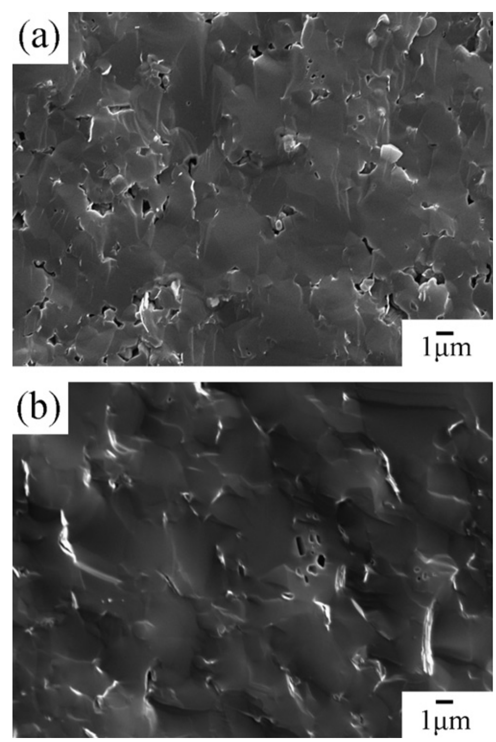

Fig. 4. SEM imagines of the fracture surface of B_4C ceramics sintered at (a) 2000 °C and (b) 2100 °C, respectively.

Table 1
Properties of the B_4C ceramics sintered at 2000 °C and 2100 °C, respectively.

Sintering temperature (°C)	Density (g/cm^3)	Relative density (%)	Flexural strength (MPa)	Hardness (GPa)	Toughness ($MPa\ m^{1/2}$)
2000	2.35	93.4	485 ± 102	29.6 ± 1.8	3.0 ± 0.3
2100	2.44	96.8	636 ± 70	30.8 ± 0.6	3.9 ± 0.1

there were only a few closed pores in the sintered bodies and the fracture mode was of transgranular type.

4. Conclusions

In summary, boron carbide ceramics with good mechanical properties have been fabricated by environmental friendly aqueous tape casting method. The main conclusions of the present work are as follows:

(1) The addition of some amount of dispersant TMAH could significantly increase the zeta potential of B_4C suspension owing to the dissociation of the TMAH, which could help to cause more negative charge on the B_4C particle surface and increase the ionic strength in the suspension. Consequently, the increase of zeta potential of the B_4C particles would be beneficial for increasing the repulsion force among particles and obtaining slurries with more stability. Moreover, the optimal pH value and the TMAH content would be in range of 6–8 and 0.5 wt%, respectively.
(2) With the addition of 18 wt% of binder (GEM02: Impranil LP RSC 1554 = 2:1), smooth, complete and defect free B_4C green tapes with good flexibility and machinability could be obtained.
(3) After sintering at 2100 °C, dense B_4C sample could be fabricated, while the relative density and the flexural strength could achieve 96.8% and 636 ± 70 MPa, respectively.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (nos. 50990301 and 51072210), Shanghai Science and Technology Committee and the State Key Laboratory of High Performance Ceramics and Superfine Microstructures.

References

[1] H.W. Kim, Y.H. Koh, H.E. Kim, Densification and mechanical properties of B_4C with Al_2O_3 as a sintering aid, Journal of the American Ceramic Society 83 (2000) 2863–2865.
[2] C.X. Liu, J.L. Sun, Erosion behaviour of B_4C-based ceramic composites, Ceramics International 36 (2010) 1297–1302.
[3] J.E. Zorzi, C.A. Perottoni, J.A.H.da Jornada, Hardness and wear resistance of B_4C ceramics prepared with several additives, Materials Letters 59 (2005) 2932–2935.
[4] F. Thevenot, Boron carbide-a comprehensive review, Journal of the European Ceramic Society 6 (1990) 205–225.
[5] H. Lee, R.F. Speyer, Pressureless sintering of boron carbide, Journal of the American Ceramic Society 86 (2003) 1468–1473.
[6] M. Bouchacourt, F. Thevenot, The correlation between the thermoelectric properties and stoichiometry in the boron carbide phase B_4C–$B_{10.5}C$, Journal of Materials Science 20 (1985) 1237–1247.
[7] Q.C. Ma, G.J. Zhang, Y.M. Kan, Y.B. Xia, P.L. Wang, Effect of additives introduced by ball milling on sintering behavior and mechanical properties of hot-pressed B_4C ceramics, Ceramics International 36 (2010) 167–171.
[8] A. Matsumoto, T. Goto, A. Kawakami, Slip casting and pressureless sintering of boron carbide and its application to the nuclear field, Journal of the Ceramic Society of Japan 112 (2004) S399–S402.
[9] J. Kiggans, T. Tiegs, F. Montgomery, M. Morrow, B. Mikijelj, A. Suman, Gelcast forming of non-oxide ceramics with reactive surfaces, in: Advances in Powder Metallurgy and Particulate Materials, vol. 2, 1999. pp. 4–19.
[10] S. Grasso, C. Hu, O. Vasylkiv, T.S. Suzuki, S. Guo, T. Nishimura, S. Yoshio, High-hardness B_4C textured by a strong magnetic field technique, Scripta Materialia 64 (2011) 256–259.
[11] Y. Qiao, Y. Liu, A. Liu, Y. Wang, Boron carbide green sheet processed by environmental friendly non-aqueous tape casting, Ceramics International 38 (2012) 2319–2324.
[12] R.E. Mistler, Tape casting: the basic process for meeting the needs of the electronics industry, American Ceramic Society Bulletin 69 (1990) 1022–1026.
[13] K.H. Zuo, D.L. Jiang, Q.L. Lin, Al_2O_3/Ni laminar ceramics shaped by tape casting and electroless plating, Journal of the American Ceramic Society 88 (2005) 2659–2661.
[14] L.L. Ren, Y.P. Zeng, D.L. Jiang, Fabrication of gradient pore TiO_2 sheets by a novel freeze-tape-casting process, Journal of the American Ceramic Society 90 (2007) 3001–3004.
[15] Y.P. Zeng, D.L. Jiang, P. Greil, Tape casting of aqueous Al_2O_3 slurries, Journal of the European Ceramic Society 20 (2000) 1691–1697.
[16] Z.H. Lv, T. Zhang, D.L. Jiang, J.X. Zhang, Q.L. Lin, Aqueous tape casting process for SiC, Ceramics International 35 (2009) 1889–1895.
[17] L. Nikzad, A. Mirhabibi, M. Vaezi, J. Javadpoor, Tape casting of graphite in non-aqueous media, Materials & Design 30 (2009) 346–352.
[18] S.L. Dole, S. Prochazka, R.H. Doremus, Microstructural coarsening during sintering of boron carbide, Journal of the American Ceramic Society 72 (1989) 958–966.
[19] J.H. Xiang, Y. Huang, Z.P. Xie, Study of gel-tape-casting process of ceramic materials, Materials Science and Engineering A – Structures 323 (2002) 336–341.
[20] J.X. Zhang, D.L. Jiang, Q.L. Lin, Aqueous processing of boron carbide powders, Journal of the Ceramic Society of Japan 116 (2008) 681–684.
[21] W. Li, P. Chen, M.Y. Gu, Y.P. Jin, Effect of TMAH on rheological behavior of SiC aqueous suspension, Journal of the European Ceramic Society 24 (2004) 3679–3684.