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Boron carbide green sheet processed by environmental friendly non-aqueous tape casting

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Abstract

An environmental friendly non-aqueous tape casting process for producing boron carbide green sheet has been discussed in the present paper. An ethanol-based formula was developed by using castor oil, single-oleic acid glycerol, polyvinyl butyral and di-n-butyl phthalate as the dispersant, wetting agents, binder and plasticizer, respectively. The influence of binding system on rheological behavior of the slurry was studied. In addition, the effects of drying condition, milling time and binding systems on green sheet were also investigated. The results indicate that the optimal composition of the boron carbide slurry is 47.0 wt.% boron carbide powder with particles size of 3.5 μm, 2.0 wt.% dispersant, 2.0 wt.% wetting agent, 39.0 wt.% EtOH, 5.0 wt.% binder and 5.0 wt.% plasticizer. The green sheet with high-quality can be obtained by the combination of the three-stage milling method and drying process conducted at room temperature without air convection. The density and tensile strength of the boron carbide green sheet are 1.64 ± 0.06 g/cm^3 and 2.66 MPa, respectively.

Keywords: A. Tape casting; Boron carbide ceramic; Sheet

1. Introduction

Boron carbide (B_4C) is widely applied in various engineering fields due to its excellent properties such as high hardness (29.1 GPa), low density (2.52 g/cm^3), chemical inertness, high melting point, and its ability to absorb neutron without forming long-lived radionuclide [1]. As the third hardest material after diamond and cubic boron nitride, B_4C is also known as black diamond extensively used as tools, control rod and shielding material [1–4]. In addition, B_4C with low density and high Young's modulus can be used in the military helicopters and similar aero-applications as a kind of excellent light-weight armor materials [5]. However, the inherent low fracture toughness of B_4C material commonly leading to the catastrophic rupture has limited its practical application.

A method has been proposed to reinforce ceramic using laminar materials by Clegg et al. [6]. In their work, a kind of SiC laminar composite materials were prepared using 0.2 mm SiC sheet as matrix and graphite sheet as separating layer. The toughness value of the laminar composite material was up to 15 MPa m$^{1/2}$, the fracture work reached 4625 J/m^2, which is dozen times higher than the fracture work of the conventional SiC ceramics. Moreover, the laminated Si_3N_4 with weak boron nitride interphases composites with work-of-fracture of 6500 J/m^2 had been developed by Liu et al. [7]. Thus, the functionally heterogeneous modulus materials can be adopted to improve fracture toughness of non-oxide ceramics.

The basic step of preparing the laminar material is to obtain green flat sheet. It is well kwon that tape casting technology is a powerful method to prepare flat and large-sized ceramic components [8–11]. This technology is commonly applied in electronic industry, although some authors have also used this to obtain structural ceramics with enhanced properties [12,13]. However, few works have been reported in literatures dealing with the preparation of B_4C sheet from its powders up to now.

This paper aims to develop a novel method to fabricate boron carbide green sheet by environmental friendly non-aqueous tape casting. The rheological behavior of slurry and the properties of green sheet were investigated substantially.

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2. Experimental

2.1. Materials

The raw powder used in this study was boron carbide ($D_{50} = 3.5$ μm, B: 80 wt.%, C: 19.4 wt.%, Fe: 0.3 wt.%, O: 0.15 wt.%, Si: 0.05 wt.%; Jingangzuan, Co., China).

2.2. Preparation of slurry for tape casting

In the present experimental condition, the tape casting slurry consisted of solvent, powder, dispersant, binder and plasticizer. To avoid competitive adsorption, the binder and plasticizer should be added after all of the others. The slurry was therefore prepared by two-stage ball milling procedure. Firstly, B_4C powders, solvent, dispersant and wetting agents were mixed together by ball milling for 12 h with nylon jar and nylon balls. Secondly, binder and plasticizer were added. Different concentrations of binder and plasticizer system were tested. Data of the powders and main organic additives used in this experiment were summarized in Table 1. The rheological behavior of the slurry was tested by a rotational rheometry (Haake AR2000ex, Karlsruhe, Germany). The measurements were performed using parallel-plate system at room temperature. The radius of the upper plate was 40 mm and a gap of 500 μm between the two parallel plates was set for all tests.

2.3. Tape casting and green sheet

Tape casting experiments were conducted by a self-made machine with a stationary container and a double-blade system. To ensure a uniform thickness of the sheet, the height of blade was adjusted by micrometer screws. Thin sheets were produced by casting the slurry on a moving carrier support. The gap between the blade and carrier support was maintained constant at 500 μm, the casting speed and shear rate was fixed at 5 mm/s and $10\ s^{-1}$, respectively. Drying was performed at room temperature without air convection.

Surface morphology of the green sheet was observed by zoom stereo microscope (SZ760 OPTEC, Chongqing, China). Microstructural observations of both sides of green sheet were performed using scanning electron microscopy (SEM, S-4800 Hitachi, Japan). The density of green sheets was measured using a hydrometer (GP-300s, Matsuhaku, Taiwan, China).

3. Results and discussion

3.1. Slurry characterization

In preparation of the slurry for tape casting, one of the most important steps is the dispersion milling procedure. In this step, to separate or hold separate the primary particles so that the binder can cover them individually, the castor oil was selected as dispersants in the present experiment.

Table 1
Data of the powder and the main organic additives used in this work.

B_4C powder	$D_{50} = 3.5$ μm; specific surface area = 4.46 $m^2\ g^{-1}$
Solvent	EtOH
Dispersants	Castor oil
Wetting agents	Single-oleic acid glycerol
Binder	Polyvinyl butyral (PVB)
Plasticizer	Di-n-butyl phthalate (DBP)

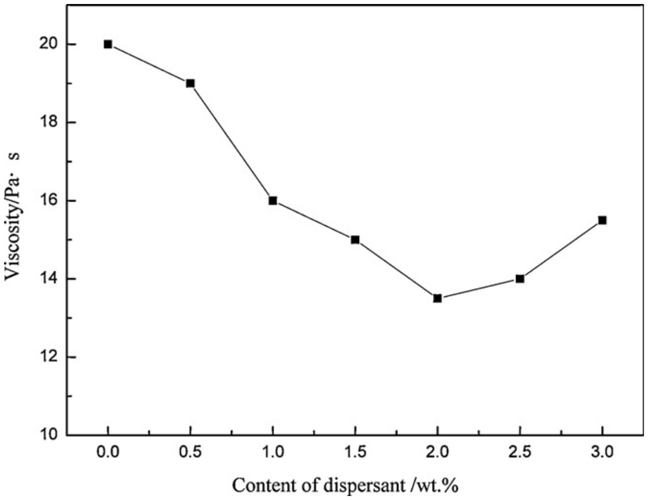

Fig. 1. Dispersant curves of 57 wt.% B_4C slurry (at a shear rate of $1\ s^{-1}$), prepared in EtOH after homogenization times of 12 h.

Fig. 1 shows the viscosity of slurry containing different dispersant contents at shear rate of $1\ s^{-1}$, prepared in EtOH after homogenization times of 12 h. It is obvious that the viscosities of the slurry decrease at first and then increase with the increasing dispersant content. The slurry containing 2.0 wt.% dispersants has the lowest viscosity. The decreasing and lower slurry viscosity implies that the particles in slurry are well dispersed.

The results of Fig. 1 are consistent with three processes called agglomeration, dispersion and flocculation. As little dispersant was added, air phase remained in the lumps of powder forming agglomerates, which led to high viscosity [14]. When the powder particles are in proximity, they often have a tendency to form loosely bound groups called flocs. The attractive force and binding force can be contributed electrostatically, by Vander Waals forces, or by a number of other inter particulate forces [15]. The higher viscosity is caused by agglomeration and flocculation when less or more dispersant are applied in the slurry [14].

In this step, primary particles need to be separated by dispersant in advance to be covered by the binder individually. Therefore, 2.0 wt.% of dispersant was chosen as the optimal one under the present experiment condition.

To investigate the influence of the slurry composition on theological properties of the slurry, several samples were prepared (Table 2).

In Table 2, the shear-thinning (P) of a slurry is characterized by the ratio of the viscosities at $1\ s^{-1}$ and $10\ s^{-1}$.

$$P = \frac{\eta(\dot{\gamma} = 1 \quad s^{-1})}{\eta(\dot{\gamma} = 10 \quad s^{-1})} \qquad (1)$$

Table 2
Composition and rheological properties of slurry.

Composition	Powder (wt.%)	EtOH (wt.%)	Dispersant (wt.%)	Wetting agents (wt.%)	Binder (wt.%)	Plasticizer (wt.%)	η (10 s^{-1}) Pa s	P
S1	57	39.0	2.0	2.0	0	0	2.555	7.957
S2	47.0	39.0	2.0	2.0	5	5	12.06	7.408
S3	46.5	38.5	2.0	2.0	6	5	9.522	5.532
S4	47.5	39.4	2.0	2.0	4	5	3.607	7.785

When $P = 1$, the viscosity is constant and the slurry presents Newtonian behavior. When $P > 1$, the bigger is P, the greater is the shear-thinning [16].

Fig. 2 shows the viscosity curves of tape casting slurry. All samples in Fig. 2 exhibit different shear-thinning behaviors: a decrease in viscosity is caused by increasing shear rate with the binder as a dominating factor. S2 exhibit much well shear-thinning behavior in the samples.

In the tape casting slurry, it is desirable that the content of organic additives keeps as low as possible. That is because the organic additives will be burnt out finally, the low amount of organic additives could reduce the risk of defect formation. Thus high B_4C powder content was desirable; it may lead to high viscosity. Meanwhile a homogeneous mass flow of slurry under the blade during the casting process must be ensured. The rheological behavior of S2, S3 and S4 all meets the needs of the tape casting, i.e. high viscosity at low shear rate (1 s^{-1}) and low viscosity at high shear rate (10 s^{-1}).

3.2. Sheet defect

The slurry with shear-thinning behavior is favorable for tape casting and will produce a smooth as well as homogeneous surface. However, cracks, bubbles and bulges could be developed within some compositions under certain conditions when the solvent was evaporated.

Fig. 3 shows surface morphology of the sheet fabricated under different condition. It can be seen from Fig. 3(a) that the surface of the green sheet by slurry S3 is rough and appears some Crow's-foot cracks. The Crow's-foot cracks are mainly originated from small bulges [15]. It maybe the slurry is not properly deflocculated before adding the PVB or a high amount of binder and plasticizer are used. Therefore the binder content should be reduced.

Moreover, Crow's-foot cracking maybe originates from bubbles (Fig. 3(b)), the bubbles are found on the bottom of the green sheet (Fig. 3(c)), but the crow-foot-shaped cracks could not been observed. Both two kinds of bubbles would be mainly caused by incomplete removal of entrapped air, which should be removed by the following degassing process. There are several ways to degas at present [15]. In our work, degassing was performed by reducing the speed of ball milling and aging time. The speed of milling was 40–80 rad/min and the aging time was 4–8 h. Two-stage milling plus degassing milling could be called as three-stage milling in this paper.

Drying is a critical stage for the tape casting. With many additives and typically multiple solvents incorporated, the behavior of the sheet during the drying process can vary greatly from slurry to slurry. When drying is performed with air convection, the cracks are found on the center of the tape along the direction of tape casting, as shown in Fig. 4. The speed that the solvent moves to the surface is much lower than that of

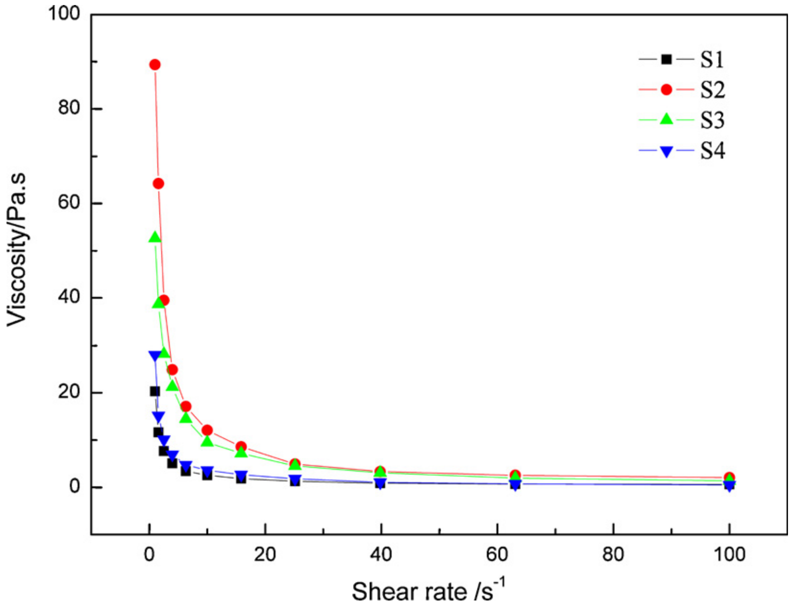

Fig. 2. Viscosity curves of tape casting slurry.

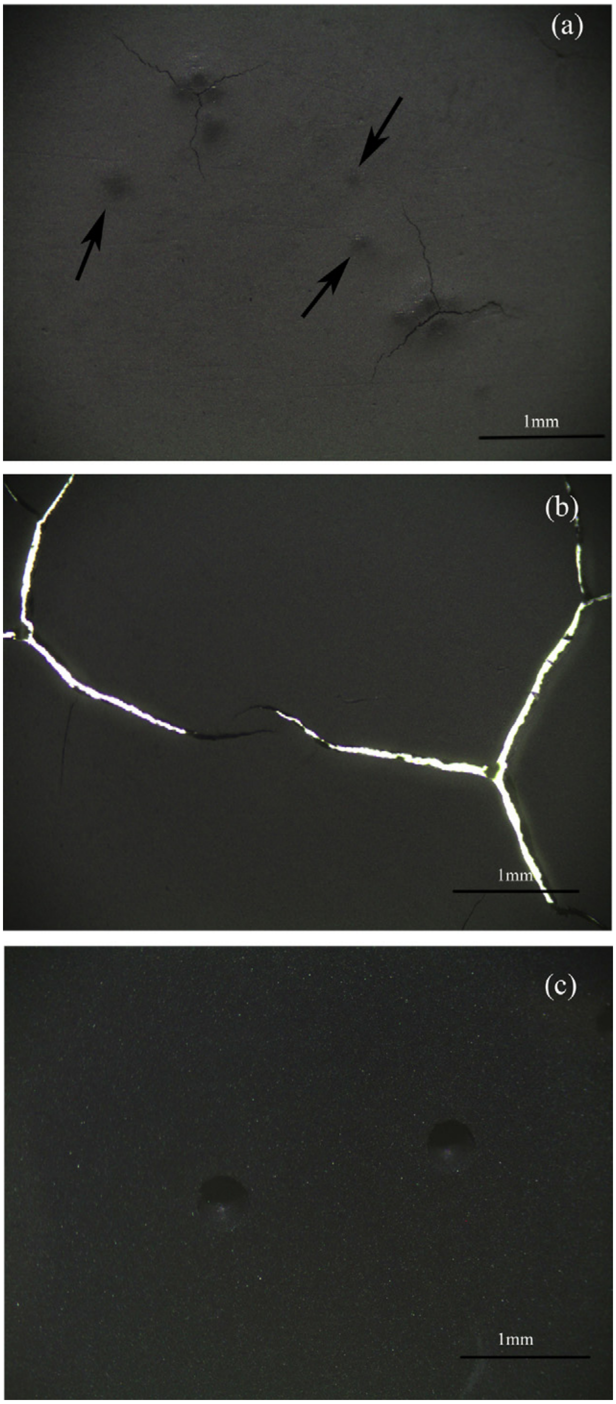

Fig. 3. Zoom stereo microscope micrograph of the surface of rough green sheet (a) Crow's-foot cracks from the small bulges; (b) Crow's-foot cracks from the small pin holes; and (c) small pin holes on the bottom surface.

evaporation with air convection. When the inter-particulate adhesion is lower than the carrier adhesion, the sheet will produce cracks from bubbles, streaks, agglomerates or inhomogeneity. When drying is performed in an airtight space, the solvent is evaporated, and is condensed at the top of airtight space, then dropped on the sheet. Therefore, the drying process is better to be performed at room temperature without air convection.

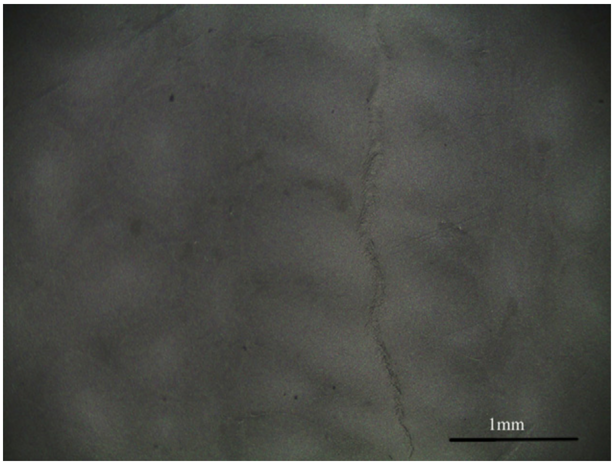

Fig. 4. Zoom stereo microscope micrograph of center cracking on cast tape.

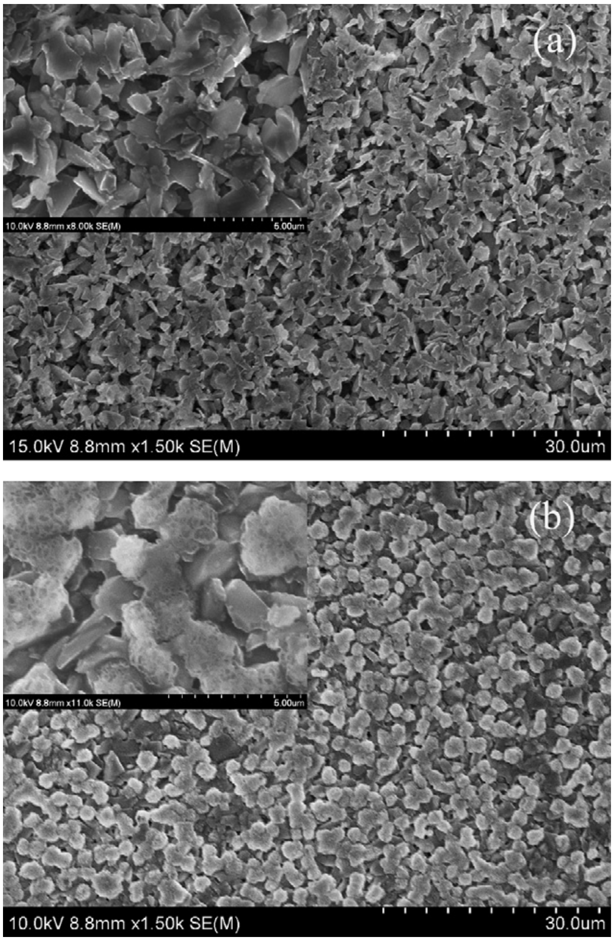

Fig. 5. SEM micrographs of green sheet surface: (a) top surface of green sheet and (b) the bottom surface of green sheet.

3.3. *Sheet release*

After being dried for 24 h, the green sheet, with thickness shrinkage of 50%, had an average thickness about 250 μm. The green sheet with silicon covered was easier to be removed from the carrier film than that sheet casted directly. However, if the oil film was too thick, it was difficult to tape casting on the film as the friction between the slurry and the film was too low. When the green sheet thickness was lower than 500 μm, Mylar film by silicon spraying is a better choice [9]. The green sheet was removed from the film by peeling at a small corner and then tore off along the direction of tape casting. Moreover, when the content of plasticizer was higher than that of binder, the sheet was difficult to release.

3.4. Green sheet characterization

3.4.1. Sheet surface

In the present experiment, the dried sheets have smooth and homogeneous surfaces without cracks. The microstructures of green sheet surface are shown in Fig. 5. The differences are found in roughness and particle arrangement between the top and the bottom surface. The top surface micrograph of the sheet shows the uniformity without agglomerate. The bottom surface is much smoother than the top one. At the same time, a network is formed by binders that stick onto the carrier film because of the plastic deformation occurred between the bottom surface and the carrier or because of the different evaporation rate of the top and the bottom sheet surface.

3.4.2. Density

In the present study, the sheets were obtained from the slurry with 5.0 wt.% plasticizer, 4.0–6.0 wt.% binder and the slurry with 5.0 wt.% binder, 4.0–6.0 wt.% plasticizer. Fig. 6 shows effects of binder and plasticizer contents on the densities of sheets. It can be seen that the sheet density increases at first by increasing the binder content (Fig. 6a). As long as the slurry was homogenous, the more content binder was, the more compact powders were. When the binder content was over 5 wt.%, the solvent was insufficient for dissolving the binder, the sheet would be inhomogeneous and the large agglomerations would be remained. The green sheet was uneven and the density varied in one sheet. The agglomerations will lead to the densities variation in different parts of the sheet.

In addition, it can be seen from Fig. 6b that the sheet density of the sheet first increases and then decreases with the plasticizer increased. Di-n-butyl was often used to soften the binder polymer chains, allowing them to stretch or deflect under an applied force [16]. It can make the rearrangement of particles become easier under the blade, thus leading to more compact sheet. However, as the plasticizer content increased continuously, the solid content decreased, then the density was reduced.

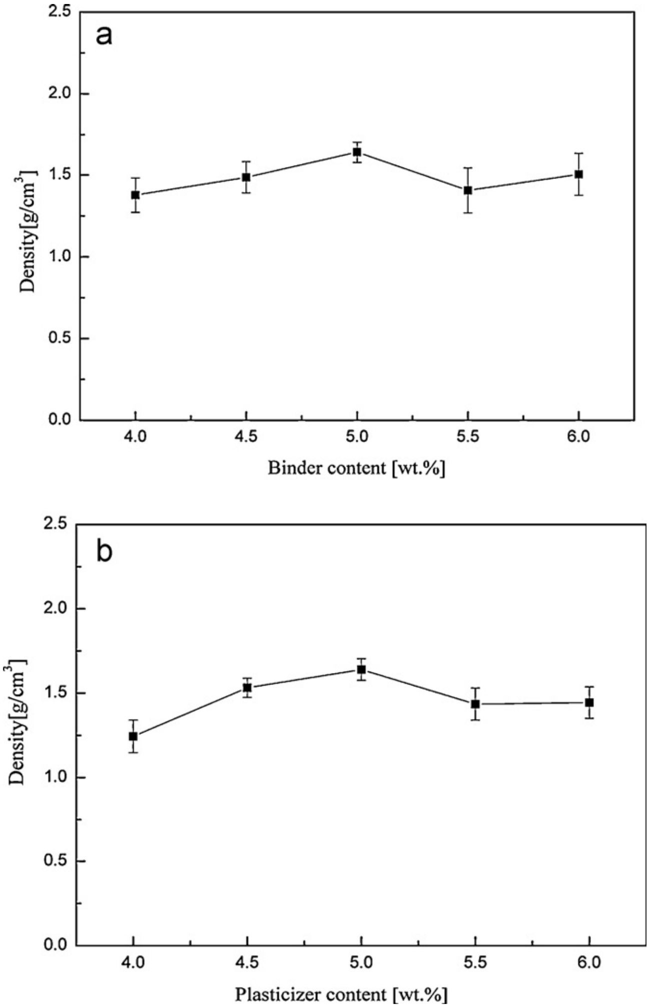

Fig. 6. The effect of binder content and plasticizer content in density of the sheets: (a) binder and (b) plasticizer.

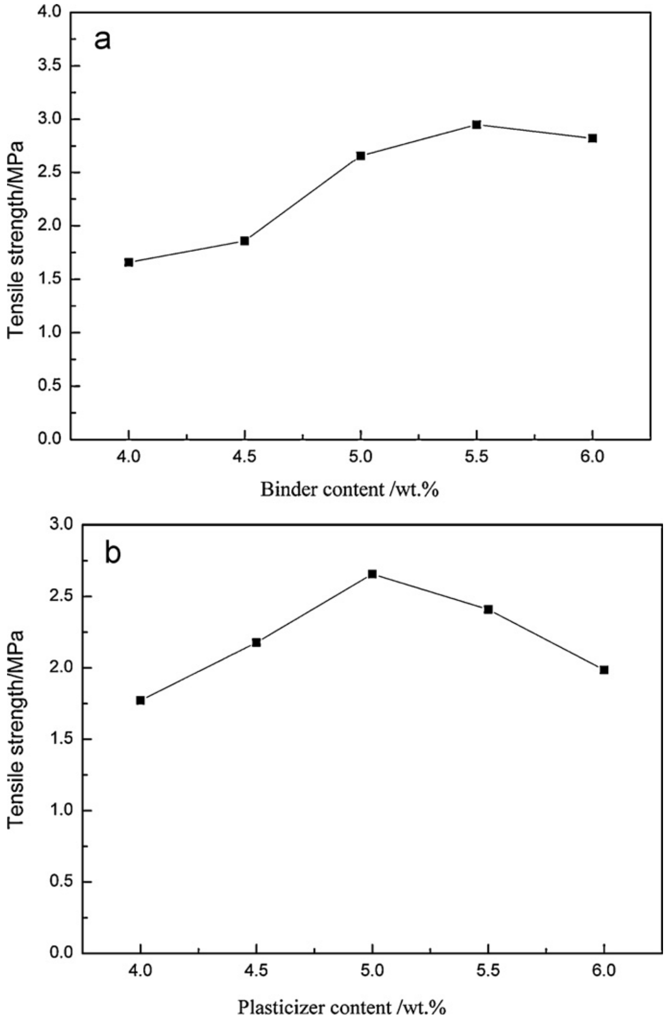

Fig. 7. The effect of binder content and plasticizer content in tensile strength of the green sheets: (a) binder and (b) plasticizer.

High relative density of the green sheet could be beneficial for the sintering of laminated B_4C ceramics. Therefore, the optimal contents of the binder and plasticizer are both 5.0 wt.%, and the relative density is 71.3%.

3.4.3. Tensile strength

Fig. 7 shows the effects of binder and plasticizer content on tensile strength of the sheets mentioned in Section 3.4.2. As the binder content increases, the sheet tensile strength might increase. From Fig. 7(a), the tensile strength decreases for the sheet with binder content up to 6.0 wt.%. It can be concluded that the binder is agglomerated and cannot dissolve into the solvent (in Fig. 7(b)), so the tensile strength decreases. When the plasticizer content increases, the tensile strength of the sheet firstly increase and then decrease. It is explained that the plasticizer can soften the binder polymer chains as mentioned above. The sheet could be easily laminated due to the good strength, so the optimal contents of the binder and plasticizer system are both 5.0 wt.%, which is agreed well with the optimal formula of density.

4. Conclusion

(1) Boron carbide green sheet were successfully produced by an environmental friendly non-aqueous tape casting process. The shear-thinning rheological behaviors of the slurry are almost the same, though small variations in composition of the system had a significant influence on the viscosity of slurry.

(2) The higher quality sheet with reduced small bubbles can be obtained by three-stage milling. Therefore the cracks caused by small bubbles were also decreasing. When the binder content is more than 5.0 wt.%, small bulges and cracking are found on tapes. Drying without convection air at room temperature could reduce the green sheet defects.

(3) The optimal composition of boron carbide green sheet is 47.0 wt.% boron carbide powder with particles size of 3.5 μm, 2.0 wt.% dispersant, 2.0 wt.% wetting agent, 39.0 wt.% EtOH, 5.0 wt.% binder and 5.0 wt.% plasticizer. The density and tensile strength of the boron carbide green sheet are 1.64 ± 0.06 g/cm^3 and 2.66 MPa, respectively. The new developed tape casting process could be used to produce laminate-structure B_4C composite with good fracture toughness.

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References

[1] F. Thevenot, Boron carbide: a comprehensive review, J. Eur. Ceram. Soc. 6 (1990) 205–225.

[2] D. Jianxin, Erosion wear of boron carbide ceramic nozzles by abrasive air jets, Mater. Sci. Eng. A 408 (2005) 227–233.

[3] C. Yanfeng, C. Yip-Wah, L. Shuyou, Boron carbide and boron carbonitride thin films as protective coatings in ultra-high density hard disk drives, Surf. Coat. Technol. 200 (2006) 4072–4077.

[4] P. Dunner, H.J. Heuvel, M. Horle, Absorber materials for control rod systems of fast breeder reactors, J. Nucl. Mater. 124 (1984) 185–194.

[5] D. Jianxin, Z. Jun, F. Yihua, D. Zeliang, Microstructure and mechanical properties of hot-pressed B_4C/(W,Ti)C ceramic composites, Ceram. Int. 28 (2002) 425–430.

[6] W.J. Clegg, K. Kendall, N.McN. Alford, J.D. Birchall, T.W. Button, A simple way to make tough ceramics, Nature 347 (1990) 455–457.

[7] H. Liu, S.H. Hsu, Fracture behavior of multilayer silicon nitride/boron nitride ceramics, J. Am. Ceram. Soc. 79 (1996) 2452–2457.

[8] J. Zhang, D. Jiang, Q. Lin, Z. Huang, Preparation of TiC ceramics through aqueous tape casting, Cream. Int. 31 (2005) 475–480.

[9] C.A. Gutierrez, R. Moreno, Tape casting of non-aqueous silicon nitride slips, J. Eur. Ceram. Soc. 20 (2000) 1527–1537.

[10] L. Zhihui, Z. Tao, Z. Dongliang, L. Qingling, Aqueous tape casting process for SiC, Ceram. Int. 35 (2009) 1889–1895.

[11] S. Biamino, A. Antonini, M. Pavese, P. Fino, C. Badini, $MoSi_2$ laminate processed by tape casting Microstructure and mechanical properties' investigation, Intermetallics 16 (2008) 758–768.

[12] T. Chartier, D. Merle, J.L. Besson, Laminar ceramic composites, J. Eur. Ceram. Soc. 15 (1995) 101–107.

[13] A.J. Sanchez-herencia, J. Gurauskis, C. Baudin, Processing of Al_2O_3/Y-TZP laminates from water-based cast tapes, Composites B37 (2006) 499–508.

[14] I. Yishihiko, Multilayered Low Temperature Cofired Ceramics (LTCC) Technology, Springer Verlag, Berlin, 2005.

[15] R.E. Mistler, E.R. Twiname, Tape Casting Theory and Practice, The American Ceramic Society, Westerville, 2000.

[16] E. Roncari, P. Pinasco, M. Nagliati, D. Sciti, Tape casting of AlN–SiC–$MoSi_2$ composites, J. Eur. Ceram. Soc. 24 (2004) 2303–2311.